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# TECHNOLOGY OF CELLULOSE ETHERS

A THEORETICAL AND PRACTICAL TREATISE ON THE  
ORIGIN, HISTORY, CHEMISTRY, MANUFACTURE, TECH-  
NICAL APPLICATION AND ANALYSIS OF THE  
ETHERIFIED CELLULOSES AND CARBOHYDRATE  
CARBOXYLATE ETHERS (ESTERIFIED CEL-  
LULOSE ETHERS, ETHERIFIED ORG-  
ANIC CELLULOSE ESTERS)

*Including*

ALKYLCELLULOSES, ARYLCELLULOSES, ARALKYLCELLULOSES,  
AS METHYLCELLULOSE, ETHYLCELLULOSE, BENZYLCELLU-  
LOSE, WITH CELLULOSE FORMATE, CELLULOSE ACE-  
TATE, THEIR SOLVENTS AND PLASTIFIERS, AS  
APPLIED TO TECHNOLOGY, PHARMACY, MEDI-  
CINE, MICROSCOPY, PHOTOGRAPHY, DEN-  
TISTRY AND THE PEACEFUL ARTS

*By*

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ESTERS," "CELLULOSE ACETATE," "CHEMICAL PATENTS  
INDEX, UNITED STATES 1915-1924."

In Five Volumes

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VOLUME ONE

HISTORICAL DEVELOPMENT OF THE CELLULOSE ETHERS

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MILLBURN NEW JERSEY

1933

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## PREFATORY STATEMENT

Some years ago a systematic effort was begun to corral in the original the widely scattered printed literature and patent information pertaining to the various activities of the carbohydrate ethers, ether-esters and allied bodies in the many fields of technical usefulness proposed for them, and to meticulously index that information as accumulated. This, supplemented by the Author's experience in the field, augmented by knowledge in the closely allied arts of the inorganic (cellulose nitrate) and organic (cellulose acetate) ester fields, when systematized and coherently grouped into the topics herein, constitutes the fundamental basis of the subject matter contained in this work; being an attempt to edit by logical succession of treatment, an aggregation of ideas, methods of procedure and experimental results represented by 13,173 separate patents issued and about 2,800 literary contributions published, bearing upon the chemistry and application of these bodies, and purporting to cover the entire published knowledge in its broadest aspects.

Every effort of inherent merit must be predicated by a predetermined logical plan. The aim of this work is to segregate the known facts under a series of 15 chapter headings, the information for more ready assimilation being subdivided into 954 separate topics, these further divided into upwards of 400 sub-topics, and supported by about 52,000 patent and literary citations in the 13,770 separately numbered appended notes to which reference is indicated. Especial effort has been made as to the accuracy and comprehensiveness of the Indices, exceeding 100,000 entries, and it is believed that inability to locate herein from the Indices the information sought, may be considered as trustworthy evidence that it is irrelevant, ephemeral or non-existent. However, it is obviously impossible without unwarranted expansion by useless repetition to correlate all the known facts concerning a chemical, process or product under a single heading, and therefore the Indices should always be consulted in endeavoring to obtain the maximum of information upon a specified subject. In the Indices, especially the Subject, no attempt at brevity has been made other than clarity with conciseness.

The work has been laid out from the angle of scientific authoritativeness and literary dignity with no attempt at fascinating readability, arrangement being by groups of affiliated subjects, and by placing cognate topics in close association. There will be found little unsupported assertion, reference to statements made and conclusions drawn being placed at the bottom of the page *on which they occur*, and not at the end of the Chapter or elsewhere necessitating search, thus preserving free-reading and continuity of the text, and assuring maximum availability of subject matter with minimum of labor in seeking additional information upon a specified subject. The work is arranged syndetically with several thousand cross-references,

and to still further assist in the ready location of information, the specific note ("n.") as well as the page is recorded in the majority of instances, thus usually locating the information within a single sentence on the page. The upwards of 52,000 patent citations indicated and excerpted herein and all reading upon some phase of one branch of technical exploitation, well illustrate the truism that there is no finality in human invention, and that human ingenuity is practically illimitable.

This work is to be regarded merely as the chronicle of a multiplicity of ideas, methods of procedure and results attained as revolving round the general subject of etherified carbohydrate bodies, and is intended merely as a *guide* for those seriously seeking information, rather than for one who may be expecting easy reading. While intended as exhaustive, it is merely indicative, and presupposes some chemical knowledge on the part of the reader. The art attempted to be corralled and encompassed within these pages is so broad, intricate and active in the multiplicity of its ramifications, that any moderately successful attempt to set forth the facts must necessarily involve an abbreviated and perhaps not always euphonious style of presentation, in order to confine the subject matter within the paginal limitation of these five volumes. It is the first published monograph on the subject insofar as aware, and like other first efforts, probably contains its quota of errors in judgment and in fact. We would appreciate attention being called to such.

The plan of this work, the "Technology of Cellulose Ethers" is as follows:—

*Chapter I.* (Vol. I, 306 pages). The advancement of any particular phase of a subject may often be best understood, extensions of existing knowledge carried forward, and future expansions more accurately predicated, by a close scrutiny of the steps of chronological advancement from the original discovery to the present day efforts at perfection. This Chapter therefore, aims at a historical summation of the origin, advancement and present position of the cellulose ether industry from the viewpoint of its systematic development, and as a statement of the steps in theory and practice from the *premiere memoire* to the close of 1932, divided for convenience into periods depending upon the relative activity of the art.

*Chapter II.* (Vol. II, 794 pages). In a manner similar to that followed in Chapter I, the chronological advancement of the organic cellulose esters typified by the cellulose acetates is taken up, these bodies having many traits in common with the carbohydrate ethers. In fact, it would be impossible to adequately describe the cellulose ether art without reference to the carbohydrate carboxylates, so intricately intermingled are they in the patent art and in pure science contributions.

*Chapter III.* (Vol. III, 82 pages). A proper understanding of a technical subject is dependent in a large measure upon the appreciation which the raw materials play in their fabrication, and the physical constants of those raw materials as applicable to the fabrication of the finished product. This Chapter gives a resume of cellulose and other carbohydrate bodies from the central thought of their adaptability and applicability for purposes of etherification.

*Chapter IV.* (Vol. III, 65 pages). Inasmuch as the normal or unmodified celluloses are seldom directly etherified, but only after the

intermediate stage of alkali treatment has been resorted to, this Chapter deals with the methods proposed for transforming carbohydrates by means of alkali treatment into that most receptive form or degree of alkalicellulose for subsequent etherification, together with the manipulative details of the various methods proposed.

*Chapter V.* (Vol. III, 51 pages). The etherifying agents employed in the transformation of cellulose, other carbohydrates and their intermediate alkali compounds into the alkyl, aryl and aralkyl carbohydrate ethers, constitute the ground covered in this Chapter.

*Chapter VI.* (Vol. III, 105 pages.) As a prelude to the commercial production of the etherified carbohydrates, are certain theoretical constants, physical behavior and chemical deportment necessary to understand, and these topics form the subject matter of this Chapter.

*Chapter VII.* (Vol. III, 67 pages.) Various manufacturing conditions for the laboratory and factory scale production of the methylated, ethylated and benzylated carbohydrate bodies, together with their solubility, plasticity, viscosity and mechanical properties are treated in this section, together with intimate details.

*Chapter VIII.* (Vol. III, 40 pages). The general subject of the production of the starch ethers, alkyl saccharides and etherified polyatomic alcohols, together with the starch ether-esters and higher carboxylates is encompassed in this division of the work.

*Chapter IX.* (Vol. III, 94 pages). The aralkyl carbohydrate compounds of which benzylcellulose is the outstanding member, together with alkyl-aralkyl-celluloses and their carboxylate compounds including miscellaneous aralkylalkylated and acylated products form the subject matter of this section.

*Chapter X.* (Vol. III, 43 pages). Mixed cellulose ethers, cellulose ether-esters, aminocelluloses, lignin ethers and the thiourethane and xanthanilid compounds are included herein.

*Chapter XI.* (Vol. III, 122 pages). The various carbohydrate ethers-esters and organically combined esters, and including certain non-inflammable, inorganically combined esters and cellulose ethers bearing inorganic radicals, are grouped in this section.

*Chapter XII.* (Vol. IV, 292 pages). Contains an enumeration and classification of Solvents, Non-solvents, Plastifying and Softening bodies exceeding 2,500 which have been proposed or made the subject of patent issuance as being advantageous in connection with the cellulose esters or ethers. No attempt at completeness has been made, the information recorded herein being merely a synopsis from which the reader interested in a particular subject is expected to consult the original literature, where fullness of record has been aimed. One reason for recording the salient facts respecting this multitude of chemical bodies which have been advocated as efficacious in some branch of cellulose derivative technology, is that as a general proposition the cellulose ethers are dissolvable in the major number of solvents which will place the nitro- and acetyl-celluloses in solution, and perhaps have as yet not been critically examined as to their suitability with the various cellulose ethers. And also for another reason that in completeness, insofar as we are aware, there exists no similar attempt to correlate in a more or less systematic manner, the large number of these bodies which have been proposed. *It only needs one of them* to impart to the cellulose ethers what camphor does to nitro-

cellulose, and the plastic cellulose ether industry is immediately placed upon a solid and enduring footing, and perhaps that one body that is so feverishly being looked for in laboratories throughout the world at the present time, is slumbering between pages 1770 and 2061 herein.

Pity the man whose mental processes are of such high viscosity that he does not dream of worlds to conquer in his particular field of endeavor. For many years we have dreamed until it has become an obsession, of attempting to reduce between covers the widely scattered data on the solvents proposed for incorporation with cellulose compounds, checking personally the recorded physical constants and preparing quantitative solubility determinations of the various dissolving bodies comprehended in this Chapter, in such an exhaustive and systematic manner that boiling point, gravity, miscibility with solvents, solubility, compatibility and dissolving avidity in unitary, binary and ternary combinations, would enable one to determine by inspection of the recorded data with a fair degree of accuracy, the relative suitability of one solvent or *solvent combination* for a specified purpose. Remember the organic cellulose esters and the cellulose ethers have no commercial value in the undissolved state. The initiation and completion of such a work is rather beyond the financial capacity of an individual unless supported by the backing of a Rockefeller Foundation or a Carnegie Institution. It appears to us as a too complicated and extensive work to be borne solely by an individual if prepared of adequate and proper comprehensiveness.

*Chapter XIII* (Vol. IV, 325 pages), and *Chapter XIV* (Vol. IV, 260 pages), comprises in 585 pages the various technical fields of usefulness which have been proposed and exploited for the various etherified carbohydrate bodies, XIII being devoted to the general art of synthetic filament formation and the fabrics and textiles made possible by aggregating in various ways a multiplicity of individual filaments.

*Chapter XV* (Vol. IV, 14 pages) contains the more simple analytical procedures in connection with the recognition and evaluation of the products previously discussed.

Indices (2665-3396, 731 pages, 101,792 separate entries), comprising *Index of Patents*, 94 pages; *Index of Names*, 98 pages; *Index of Subjects*, 539 pages. For Summaries, see pages 2665, 2759, 2857.

In order to reduce the pages to the minimum without sacrificing clarity, use has freely been made of dashes in the description of homologous and inter-related compounds, and these dashes should be critically scrutinized. For example, the sentence beginning the last paragraph of page 304 enumerates 108 separate compounds, and the same number of cards were required for the indexing of the sentence. All degrees (°) are Centigrade unless otherwise stated. For facility of checking literary references, the list of Abbreviations of Literature are inserted in Volumes I to IV inclusive.

This work is linked up with our previous volumes in the cellulose derivative field in this manner: In 1911 appeared "Nitrocellulose Industry" in two volumes of 1239 pages, being the first general survey of the technical applications of the cellulose nitrates in the peaceful arts, and was followed in 1915 by the 578 page work on "Cellulose Acetate," as Vol. VIII of a contemplated exhaustive work on the entire technics of cellulose technology. The foundation for this work



was laid in 1921 by the issuance of the five volumes, "Technology of Cellulose Esters," of 3708 pages, of which the present five volumes are a companion series, being addressed exclusively to the combination of cellulose with organic acid radicals, or the etherified celluloses. Meanwhile there has been published two volumes in 2094 pages of a projected five-volume work of upwards of 5000 pages of an Index of United States Chemical Patents for the period 1915-1924 inclusive.

The Author has been fortunate in having associated with him for over twenty years, Leo Rutstein, whose skill in the art of literary and patent searching, and in the mechanics of book production, is obvious in the Author's earlier works. In addition, it is a pleasure to acknowledge the assistance of our little group of co-workers, in their relative seigniority being Misses Lydia Englander, Evelyn L. Philips, Mae T. Forbringer, Clara H. Lewis, Charlotte Englander and Frances L. Philips, and if merit there be in this work, to them in a large measure, does the credit belong. L. Englander was primarily responsible for the Index of Names, E. Philips that of the Subjects, M. Forbringer of the Patents, and C. Lewis the References to Literature, and jointly the *labor* of arranging, checking and writing the major portion of the 13,770 separately numbered notes contained herein. The 50,394 entries comprising the Index of Subjects were transcribed on cards by C. Lewis, and classified and filed by E. Philips. In the interpretation of intricate legal points involved in issued patents and the File Wrappers of which they are a part, we have been fortunate in being able to take advantage of the knowledge and experience in this field of Hugo E. Weisberger, B. S., M. A., Chem. E., L.L.B. De Witt Bailey Bell, M. S., has revised the sections dealing with the combination of cellulose derivatives with various rubber products, and Waite Worden compiled the Table of Summaries.

Grateful appreciation is acknowledged to the Newark Printing Company and to Nathaniel Freiman, the Treasurer; to Messrs. Winfield H. Scott and J. Van Cleve Scott, linotypers, and George Henry, make-up—master craftsmen in their art—upon whom the responsibility has devolved of transforming the manuscript into the completed printed page of what must be conceded as an unusually difficult and intricate piece of typography.

A handwritten signature in dark ink, reading "Edw. C. Worden, I." The signature is written in a cursive style with a large, sweeping initial 'E' and a long, trailing flourish at the end.

MILLBURN, NEW JERSEY  
February 15, 1933

## TABLE OF SUMMARIES

Compiled by Waite Worden

Chapt.	Pages	Topics	Foot Notes	Patents	References to Literature
I	306	17	1507	2689	3,135
II	794	26	4995	7565	21547
III	82	30	466	936	1128
IV	65	18	248	560	945
V	51	37	347	734	1102
VI	105	53	240	766	848
VII	67	50	157	348	933
VIII	40	54	263	679	1053
IX	94	45	239	749	757
X	43	31	111	556	1250
XI	122	88	396	833	1404
XII	292	276	2087	7489	6800
XIII	325	151	1346	11234	5746
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# LIST OF ABBREVIATIONS TO LITERATURE

Prepared by Clara Harmon Lewis

A. and N J.	Army and Naval Journal
Aarau, Archiv der Med.	Archiv. der Medizin, Chirurgie, und Pharmazie
Aarau, Mitth.	Mittheilungen des Aargauischen Naturforschenden Gesellschaft
Abbeville, Bull. Soc Linn.	Compte Rendu et Bulletin de la Société Linneenne du Nord de la France
Abbeville, Mem. Soc Emul	Memoires de la Société d'Emulation d'Abbeville
Abeille, J.	L'Abeille, Journal d'Entomologie
Abeille mem	L'Abeille memoires d'Entomologie
Abeille Soc	(Publications de la Soc Entomologie de France ) LaAbeille Journal de Entomologie
Acad.	Memoires de l'Academie des Sciences
Acad Caes Leop. Nova Acta	Nova Acta physico-medica Academiae Caes Leopoldino-Carolinae Naturae Curiosorum
Acad Natur Curios Nova Acta	Nova Acta Academiae Caesareae Leopoldino-Carolinae Germanicae Naturae Curiosorum
Acireale Accad Atti	Atti e Rendiconti dell' Accademia di Scienze, Lettere e Arti dei Zelanti e PP. dello Studio di Acireale
Acireale, Soc Ital Micro Boll	Bollettino della Societa Italiana dei Microscopisti
Acquoy, Tijdschrift	Tijdschrift voor Wis-, Natuur-, en Wertuigkunde
Acta Math	Acta Mathematica
Actes Soc. Helvetique	Actes de la Société Helvetique des Sciences Naturelles
Adansonis	Recueil d'observations botaniques
Adelaide Phil Soc Trans	Transactions and Proceedings and Report of the Philosophical Society of Adchade, South Australia
Aeronaut J.	The Aeronautical Journal
Aeronaut Soc Reports	Annual Reports of the Aeronautical Society of Great Britain
Aeronaute	L'Aeronaute bulletin mensuel international de la Navigation Aerienne
Afhandl Fysik	Afhandlingar i Fysik, Kemi, och Mineralogi
African Assoc Proc	Proceedings of the African Association for promoting the Discovery of the Interior Parts of Africa
Agen Soc. Agric. Recueil	Recueil des Travaux de la Société d'Agriculture, Sciences, et Arts d'Agen
Agram, Program Gymnas	Program des k. k. Akademischen Gymnasiums zu Agram
Agric. Gaz.	The Agricultural Gazette
Agric Gaz. N. S Wales	Agricultural Gazette of New South Wales, The
Agric. J. India	Agricultural Journal of India
Agric. Ledg	Agricultural Ledger
Agric. Soc. J.	The Journal of the Royal Agricultural Society of England
Agric. Stud. Gaz.	Agricultural Students' Gazette A Quarterly Journal edited by Students at the College, Cirencester
Agron. Ztg.	Agronomische Zeitung
Aix, Acad. Mem.	Recueil de Memoires de la Société des Amis des Sciences, des Lettres, de l'Agricultur, et des Arts a Aix

Albany Inst. Proc.	Proceedings of the Albany Institute
Albany Inst. Trans.	Transactions of the Albany Institute
Alger. Bull. Soc. Climat.	Bulletin de la Société de Climatologie Algérienne
Alk.	Alkohol
Allelod. Soc. Trans.	The transaction of the Allelodidactic Society
Allg. Berg. Ztg.	Allgemeine berg- und huttenmannische Zeitung
Allg. Bot. Zts.	Allgemeine Botanische Zeitschrift für Systematik, Floristik, Pflanzengeographie, etc.
Allg. Deut. Naturhist. Ztg.	Allgemeine Deutsche naturhistorische Zeitung
Allg. Deut. Ornith. Ges.	See J. Ornith.
Allg. Fischerei Ztg.	Allgemeine Fischerei Zeitung
Allg. Forst- und Jagd-Zts.	Allgemeine Forst- und Jagd-Zeitung
Allg. Gerber-Ztg.	Allgemeine Gerber-Zeitung
Allg. Schweiz. Ges. Gesam. Naturwiss.	See Zürich, Schweiz. Ges. N. Denkschr.
Allg. Syn. Suikerfab.	Algemeen Syndicat van Suikerfabrikanten in Nederl. - Indie With Arch-Suikerind, etc.
Allg. Zts. Bierbr. Malz-fabr.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation
Allier, Bull. Soc. Emul.	Bulletin de la Société d'Émulation du département de l'Allier: Sciences, Arts, et Belles-Lettres
Alpina	Alpina, eine Schrift der genauen Kenntniss der Alpen gewidmet, von Carl Ulisses von Salis und J. R. Steinmueller
Altenburg Mitth.	Mittheilungen aus dem Osterlande, herausgegeben von der Naturforschenden Gesellschaft zu Altenburg
Amat. Mechan. Soc. J.	The (Quarterly) Journal of the Amateur Mechanical Society
Amer. Acad. Mem.	Memoirs of the American Academy of Arts and Sciences
Amer. Acad. Proc.	Proceedings of the American Academy of Arts and Sciences
Amer. Agric.	American Agriculturist
Amer. Ann. Phot.	American Annual of Photography
Amer. Apoth. Ztg.	Deutsch-Amerikanische Apotheker Zeitung
Amer. Artisan	American Artisan
Amer. Assoc. Proc.	Proceedings of the American Association for the Advancement of Science
Amer. Brewers Rev.	American Brewers Review
Amer. Builder	The American Builder
Amer. Chem. J.	American Chemical Journal
Amer. Chemist	American Chemist
Amer. Drug.	American Druggist and Pharmaceutical Record
Amer. Electrochem. Soc.	American Electrochemical Society
Amer. Engin. & Railroad J.	American Engineer (Car Builder), and Railroad Journal
Amer. Ethnol. Soc. Trans.	Transactions of the American Ethnological Society
Amer. Entom. Soc. Trans.	Transactions of the American Entomological Society and Proceedings of the Entomological Section of the Academy of Natural Sciences
Amer. Fertilizer	American Fertilizer, The
Amer. Food J.	American Food Journal
Amer. Gas Light J.	American Gas Light Journal, The
Amer. Geogr. Soc. Bull.	Bulletin of the American Geographical and Statistical Society
Amer. Geogr. Soc. J.	Journal American Geographical Society, New York
Amer. Geogr. Soc. Proc.	Proceedings of the American Geographical and Statistical Society of New York

Amer. Geol. and Nat. As- soc Reports	Reports of the Meetings of the Association of American Geologists and Naturalists at Philadelphia
Amer. J. Conchol	American Journal of Conchology
Amer. J. Dent Sci.	American Journal of Dental Science
Am. J. Math	American Journal of Mathematics
Amer. J. Med. Sci	American Journal of the Medical Sciences
Amer. J. Otol.	The American Journal of Otology
Amer. J. Pharm	American Journal of Pharmacy
Amer. J. Physiol	The American Journal of Physiology
Amer. J. Physiol, Boston	American Journal of Physiology, Boston
Amer. J. Psychol	The American Journal of Psychology
Amer. J. Pub Health	American Journal of Public Health
Amer. J. Sci	The American Journal of Science
Amer. Mach	American Machinist
Amer. Math Soc.	See N. Y. Amer. Math. Soc.
Amer. Med	American Medicine
Amer. Med Assoc. Trans.	Transactions of the American Medical Association
Amer. Med. Phil. Reg.	The American Medical and Philosophical Register, or Annals of Medicine, Natural History, Agriculture, and the Arts
Amer. Med. Recorder	American Medical Recorder
Amer. Meteorol. J.	American Meteorological Journal
Amer. Micro. J.	The American Quarterly Microscopical Journal With which is also published the Transaction of the New York Microscopical Society
Amer. Micro. Soc. Proc.	Proceedings of the American Microscopical Society
Amer. Micro. Soc. Trans.	Transactions of the American Microscopical Society
Amer. Mineral. J.	The American Mineralogical Journal
Amer. Min. Gaz.	The American Mining Gazette and Geological Magazine
Amer. Monthly Micro. J.	American Monthly Microscopical Journal
Amer. Mus. Bull.	Bulletin of the American Museum of Natural History
Amer. Mus. Mem.	Memoirs of the American Museum of Natural History
Amer. Natur.	American Naturalist
Amer. Ophthalm. Soc. Trans.	Transactions of the American Ophthalmological Society
American Perfumer	American Perfumer and Essential Oil Review, The
Amer. Phil. Soc. Proc.	Proceedings of the American Philosophical Society held at Philadelphia
Amer. Phil. Soc. Trans.	Transactions of the American Philosophical Society, held at Philadelphia, for promoting useful knowledge
Amer. Phot.	American Photography
Amer. Poly. J.	The American Polytechnic Journal
Amer. Quart. J. Agric.	American Quarterly Journal of Agriculture and Science
Amer. Reports State Entom.	See Ill., Mass., Mo., N. Y.
Amer. Soc. Agr. Sci. Proc.	Proceedings of the Society for the Promotion of Agricultural Science
Amer. Soc. Civ. Engin. Trans.	Transactions of the American Society of Civil Engineers
Amer. Soc. Micro. Proc.	Proceedings of the American Society of Microscopists
Amer. Sugar Ind.	American Sugar Industry and Beet Sugar Gazette, The
Amer. Vet. Rev., N. Y.	American Veterinary Review, N. Y.
Amherst Agric. Sta. Re- port	Annual Report of the State Agricultural Experiment Stations, at Amherst, Mass.
Amici, Giorno Loscano	Giornale Loscano di Scienze mediche, fisiche e naturali
Amiens Acad. Sci. Mem.	Memoirs de l'Academie des Sciences, des Lettres et des Arts d'Amiens

Ammon, Monatschr. Med	Monatschrift für Medecin, Augenheilkunde, und Chirurgie
Ammon, Zts Ophthalm. Amsterdam	Zeitschrift für die Ophthalmologie Werken van het Genootschap ter Bevordering der Natuur-, Geneesen Heelkunde. See Maandbl Nat.
Amsterdam, Akad. Jaarb	Jaarboek van de koninklijke Akademie van Wetenschappen gevestigd te Amsterdam
Amsterdam, Akad. Proc.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings of the Section of Sciences
Amsterdam, Akad. Verh	Verhandelingen der koninklijke Akademie van Wetenschap
Amsterdam, Akad. Versl Mededeel.	Verslagen en Mededeelingen der Koninklijke Akademie van Wetenschappen. Afdeling Naturkunde
Amsterdam, Akad. Wet Proc.	Processen-Verbaal van de gewone Vergaderingen der Koninklijke Akademie van Wetenschappen Afdeling Naturkunde
Amsterdam, Archief Wisk Genoots.	Archief uitgegeven door het Wiskundig Genootschap
Amsterdam Bijdr. Dierk.	Bijdragen tot de Dierkunde uitgegeven door the (Koninklijk Zoologisch) Genootschap Natura Artis Magistra, te Amsterdam
Amsterdam, Bull. Congr Bot.	Bulletin du Congrès International de Botanique et d'Horticulture réuni à Amsterdam
Amsterdam Congr. Bot Actes	Actes du Congrès International de Botanistes, d'Horticulteurs tenu à Amsterdam, en 1877
Amsterdam Genootsch. "Natura Artis Magistra"	See Amsterdam Bijdr. Dierk
Amsterdam Genootsch Nat., Genees- en Heel- kunde	See Maandbl Nat
Amsterdam, Het Inst	Het Instituut
Amsterdam, Mengelwerk	Mengelwerk van uitgeleezene en andere Wisen Natuurkundige Verhandelingen
Amsterdam, Nieuw. Verh	Nieuwe Verhandelingen der eerste Klasse van het Koninklijk Nederlandsche Instituut van Wetenschappen, en Schoone Kunsten te Amsterdam
Amsterdam, Nieuw. Wis Voorstel.	Verzameling van nieuwe wiskundige Voorstellen door de Leden van het Wiskundig Genootschap, onder de zinspreuk <i>Een onvermoeide arbeid komt alles te boven</i> , elkander tot onderlinge oefening opgegeven
Amsterdam Nederl. Aandr. Genootsch. Tijdschr	Tijdschrift van het (Kon.) Nederlandsch. Aardrijkskundig Genootschap, gevestigd te Amsterdam
Amsterdam, Onderz. Phys Lab.	Onderzoekingen gedaan in het Physiologisch Laboratorium van de Doortluchtige en Klinische Scholen te Amsterdam
Amsterdam, Tijdschr Natuurk. Wetens	Tijdschrift voor Natuurkundige Wetenschappen en Kunsten
Amsterdam, Tijdschr. Wis Natuurk. Wetens.	Tijdschrift voor de Wis- en Natuurkundige Wetenschappen, Letterkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verh.	Verhandelingen der Eerste Klasse van het Koninklijk Nederlandsche Instituut van Wetenschappen, Letterkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verh. Ge- noots. Geneesk.	Verhandelingen van het Genootschap ter Bevordering der Geneesen Heelkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verzam. Ber. Navig.	Verzameling van Berichten over eenige onderwerpen des Navigatie

Amsterdam Zool. Genootsch. "Natura Artis Magistra"	See Nederl. Tijdschr. Dierk.
Anales agroa.	Anales Agronomicos
Anales fis. quim	Anales de la sociedad espanola de fisica y quimica
Anales inst med nacional	Anales del instituto medico nacional
Anales Minería Mex.	Anales de la Minería Mexicana, Revista de Minas
Analyst	The Analyst, including the Proceedings of the Society of Public Analysts
Anat.	Anatomie
Anat. Anz.	Anatomischer Anzeiger. Centralblatt für die Gesamte Wissenschaftliche Anatomie (Amtliches Organ der Anatomischen Gesellschaft)
Anat. Ges	See Anat. Anz.
Anat. Hefte	Anatomische Hefte. Referate und Beiträge (Beiträge und Referate) zur Anatomie und Entwicklungsgeschichte
Anat. Soc. Proc.	See J. Anat. Physiol.
Anat. Studien	Anatomische Studien
Angers Acad. Sci. Mem	Mémoires de l'Académie des Sciences et Belles-Lettres d'Angers
Angers, Ann. Soc. Linn	Annales de la Société Linneenne du département de Maine et Loire
Angers, Mem. Soc. Agric.	Mémoires de la Société d'Agriculture, Sciences, et Arts
Angers, Soc. Sci. Bull.	Bulletin de la Société d'Études Scientifiques d'Angers
Ann.	Liebig's Annalen der Chemie
Ann. Bot.	Annals of Botany
Ann. Chim.	Annales de Chimie
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie
Ann. chim. farm.	Annali di Chimica e di farmacologia
Ann. Chim. Phys.	Annales de Chimie et de Physique
Ann. Chimica	Annali di Chimica (Medico-Farmaceutica e di Farmacologia)
Ann. Conduct. Ponts et Chauss.	Annales des Conducteurs des Ponts et Chaussées et des Gardes-Mines
Ann. Conserv. Arts et Met.	Annales du Conservatoire des Arts et Métiers
Ann. Dermatol.	Annales de Dermatologie et de Syphiligraphie
Ann. École norm.	Annales scientifiques de l'École Normale supérieure (L. Pasteur)
Ann. Falsif.	Annales des Falsifications
Ann. Farm. Chim.	Annali di Farmacoterapia e Chimica (Biologica)
Ann. Fis. Chim.	Annali di Fisica, Chimica, etc.
Ann. Génie Civil	Annales du Génie Civil
Ann. Gén. Sci. Phys.	Annales générales des Sciences Physiques
Ann. Geogr.	Annales de Géographie
Ann. Hydrogr.	Annales Hydrographiques
Ann. Hydrogr. Mar. Met.	Annalen der Hydrographie und Maritimen Meteorologie. Organ des Hydrographischen Bureaus (Amtes) und der Deutschen Seewarte
Ann. hyg. pub.	Annales d'hygiène publique
Ann. Ind.	Annales industrielles, par Friedreau, etc.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur
Ann. Landw.	Annalen der Landwirtschaft in den K. Staaten
Ann. Landw. Wochenbl.	Annalen der Landwirtschaft, Wochenblatt
Ann. Mag. Natur. Hist.	The Annals and Magazine of Natural History, including Zoology, Botany and Geology

Ann. Matemat.	Annali di Matematica pura ed applicata
Ann. Math.	Annals of Mathematics
Ann. Med.	Annali di Medicina
Ann Med. Psychol.	Annales medico-psychologiques; Journal de l'anatomie, Physiologie, etc., du systeme nerveux
Ann Med. Surg.	Annals of Medicine and Surgery, or Records of the occurring Improvements and Discoveries in Medicine, Surgery, and their immediately connected Arts and Sciences
Ann Microgr.	Annales de Micrographie specialement consacrees a la Bacteriologie, aux Protophytes et aux Protozoaires
Ann Mines	Annales des Mines . redigees et publiees sous l'Autorisation du Ministre des Travaux Publics
Ann Museo Ind Ital.	Annali del R Museo Industriale Italiano
Ann Natur. Hist.	Annals of Natural History
Ann. Oculist	Annales d'Oculistique et de Gynecologie
Ann. Pharm.	Annals of Pharmacy
Ann Pharm Louvain	Annales de Pharmacie, Louvain
Ann. Phil.	Annals of Philosophy
Ann Phys.	Annalen der Physik
Ann Phys. Chem.	Annalen der Physik und Chemie
Ann Ponts et Chauss.	Annales des Ponts et Chaussées
Ann. R. Staz. Chim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma
Ann. Rep., U. S. Dept Agric.	Annual Report of the United States Department of Agriculture
Ann sci agron.	Annales de la science agronomique francaise et étrangère
Ann. Sci Bot. Nat.	Annales des Sciences Naturelles, Botanique
Ann Sci Lomb. Veneto	Annali delle Scienze del Regno Lombardo-Veneto
Ann Sci. Nat.	Annales des Sciences Naturelles Botanique Zoologie et Paleontologie, comprenant l'Anatomic, la Physiologie, la Classification et l'Histoire Naturelle des Animaux
Ann Sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy
Ann Scott. Natur Hist	The Annals of Scottish Natural History
Ann Surg.	Annals of Surgery
Ann. Storia Natur.	Annali di Storia Naturale
Ann Telegr.	Annales Telegraphiques
Annab -Buchh. Ver. Na-turk. Ber	Bericht uber den Annaberg-Buchholzer Verein fur Naturkunde
Annab -Buchh. Ver Na-turk Jahr	Jahresbericht des Annaberg-Buchholzer Vereins fur Naturkunde
Annaes Sci Natur.	Annaes de Sciencias Naturaes
Année Biol.	L'Année Biologique Comptes Rendus annuels des Travaux de Biologie Generale
Annot. Zool Jap.	Annotationes Zoologicae Japonenses, Auspiciis Societatis Zoologicae Tokyonensis seriatim editae
Annuaire Ancienne Normandie	Annuaire des cinq Departements de l'Ancienne Normandie, par l'Association Normandie
Annuaire Inst. Provinces	Annuaire de l'Institut des Provinces, des Societes Savantes, et des Congres Scientifiques
Annuaire met. France	Annuaire Meteorologique de la France
Annuaire Mines Russie	Annuaire du Journal des Mines de Russie
Anthropol. (Paris)	Materiaux pour l'Histoire de l'Homme. Revue d'Anthropologie. Revue d'Ethnographie reunies.
Anthropol. Congr	See Congr. Int. Anthropol. C. R.
Anthropol. Inst. J.	The Journal of the Anthropological Institute of Great Britain and Ireland

Anthropol Rev	The Anthropological Review
Anthropol Soc Mem	Memoirs read before the Anthropological Society of London
Antwerpen, Verh Genoots	Verhandelingen van het Genootschap "Occidit qui non servat"
Oce qui non	
Anvers, Ann Soc Med.	Annales de la Societe de Medecine d'Anvers
Anvers, Congr. Sci Geogr	Compte-Rendu du Congres des Sciences Geographiques, Cosmographiques et Commerciales
Anvers, J. Pharm	Journal de Pharmacie, publ par la Soc de Pharmacie d'Anvers
Apoth Ztg	Apotheker Zeitung, Berlin
Apothecary	Apothecary, Boston
Appreturzeitung	Appreturzeitung
Apt, Ann Soc Sci.	Annales de la Societe litteraire, scientifique et artistique d'Art (Vaucluse)
Aquila	Aquila A Magyar Ornithologiai Központ Folyoirata. Periodical of Ornithology
Arb Kais Gesundheits	Arbeiten aus dem kaiserlichen Gesundheitsamte, Berlin
Arb pharm Inst, D Univ. Berlin	Arbeiten aus dem pharmazeutischen Institut der Universität Berlin
Arcachon Soc Sci Stat Zool Trav	Société Scientifique et Station Zoologique d'Arcachon
Arcetri Oss Pubbl	See Firenze R Ist Pubbl (Arcetri Oss)
Archief Suikerind	Archief Suikerindustrie in Nederlandsch-Indie
Archief Wisk Genoots	Archief uitgegeven door het Wiskundig Genootschap
Archit and Eng.	Architect and Engineer
Archiv Agriculturchem	See Hermbstadt
Archiv Anat Micro	Archives d'Anatomie Microscopique
Archiv. Anat Physiol	Archiv. fur Anatomie, Physiologie und wissenschaftliche Medizin
Archiv Anthropol.	Archiv fur Anthropologie. Organ der deutschen Gesellschaft fur Anthropologie, Ethnologie und Urgeschichte
Archiv Anthropol Etnol	Archivio per l'Anthropologia e la Etnologia
Archiv Augenheilk	Archiv fur Augenheilkunde
Archiv. Augen-. Ohrenheilk	Archiv fur Augen- und Ohrenheilkunde
Archiv. belges méd mil.	Archives belges de médecine militaire
Archiv. Biol	Archives de Biologie
Archiv. Bot Nord France	Archives Botaniques du Nord de la France
Archiv Chem Mikros.	Archiv Chemie und Mikroskopie
Archiv. Cosmol	Archives cosmologiques Revue des Sciences Naturelles, avec leurs applications a la Medecine, a l'Agriculture, aux Arts, et a l'Industrie
Archiv. Dent.	Archives of Dentistry A record of Dental knowledge, medical, surgical, microscopical, chemical, and mechanical
Archiv. Elect	Archives de l'Electricite
Archiv. Entwickl. Organ.	Archiv fur Entwicklungsmechanik der Organismen
Archiv exper. Path Pharm.	Archiv fur experimentelle Pathologie und Pharmakologie
Archiv. Farmacol sper. Roma	Archivio di Farmacologia sperimentale e Scienze affini Roma
Archiv. fisiol	Archivio di fisiologia
Archiv gen Med.	Archives generales de Medecine
Archiv. ges. Physiol	Archiv fur die gesammte Physiologie des Menschen und der Thiere (Pfluger)
Archiv. Heilk.	Archiv der Heilkunde

Archiv. Hyg.	Archiv. fur Hygiene
Archiv. Internal Med.	Archives of Internal Medicine
Archiv. intl. pharmacodyn.	Archives internationales de pharmacodynamie et de thereapie
Archiv. Ital. Biol.	Archives Italiennes de Biologie Revues, Résumés Reproductions des Travaux Scientifiques Italiens
Archiv. Kinderheilk	Archiv. fur Kinderheilkunde
Archiv. Math. Naturvid.	Archiv. for Mathematik og Naturvidenskab
Archiv. Math. Phys.	Archiv. der Mathematik und Physik
Archiv. Med.	Archives of Medicine
Archiv. Med. comparee.	See Rayer
Archiv. med exp.	Archives de medicine experimentale et d'anatomie pathologique
Archiv. Med Navale	Archives de Medecine Navale (et Coloniale)
Archiv. Med. Pharm. Militair.	Archives de Medecine et de Pharmacie Militaires
Archiv. Mikro Anat.	Archiv. fur Mikroskopische Anatomie (und Entwicklungsgeschichte)
Archiv. Miss. Sci	Archives des Missions Scientifiques et Litteraires
Archiv. Naturgesch	Archiv. fur Naturgeschichte
Archiv. Naturk. (Dorpat)	Archiv. fur die Naturkunde Liv-, Ehst- und Kur-lands Herausgegeben von der Dorpater Naturforscher-Gesellschaft
Archiv. Neerland.	Archives Neerlandaises des Sciences Exactes et Naturelles publiees par la Societe Hollandaise des Sciences a Harlem
Archiv. Ohrenheilk.	Archiv fur Ohrenheilkunde
Archiv. Ophthalm	Albrecht von Graefe's Archiv fur Ophthalmologie
Archiv. Ophthalm Otol	Archives of Ophthalmology and Otology
Archiv. Otol	Archives of Otology
Archiv. Parasit.	Archives de Parasitologie
Archiv. path Anat.	Archiv fur pathologische Anatomie und Physiologie und fur klinische Medizin (Virchow's)
Archiv. Pharm.	Archiv. der Pharmacie, Archiv des Apothekervereins im nordlichen Deutschland
Archiv Pharm og Chemi	Archiv. de Pharmaci og Chemi, Copenhagen
Archiv. Physiol	Archives de Physiologie Normale et Pathologique
Archiv. Psychiatr	Archiv fur Psychiatrie und Nervenkrankheiten
Archiv. Sci	Archives of Science and Transactions of the Orleans County Society of Natural Sciences
Archiv. sci med.	Archivio per les scienze mediche
Archiv. Sci. Phys. Nat.	Bibliothèque Universelle Archives des Sciences Physiques et Naturelles
Archiv. Sci Pract. Med.	Archives of Scientific and Practical Medicine
Archiv. Slaves Biol.	Archives Slaves de Biologie
Archiv. Verdauungs-krankh	Archiv fur Verdauungs-krankheiten
Archiv. Wiss Heilk.	Archiv. des Vereins fur gemeinschaftliche Arbeiten zur Forderung der wissenschaftlichen Heilkunde
Archiv. Wiss. Prakt Thierheilk.	Archiv fur wissenschaftliche und praktische Thierheilkunde
Archiv. Zool. Anat. Fis	Archivio per la Zoologia, l'Anatomia, e la Fisiologia
Archiv. Zool. Exper.	Archives de Zoologie Experimentale et Generale
Arceuil, Mem. Phys.	Memoires de Physique et de Chimie de la Societe d'Arceuil
Argent. Inst. Geogr. Bol.	Boletin del Instituto Geografico Argentino
Argent. P.	Argentine Patent
Argent Soc. Ci. An.	Anales de la Sociedad Cientifica Argentina



Arkiv Kemi, Mineral Geol.	Arkiv for Kemi, Mineralogi och Geologi
Arkiv Math. Astron Fysik	Arkiv for Mathematik Astronomi och Fysik
Armagh Nat Hist & Phil Soc.	See Irish Natlist
Arms and Expl	Arms and Explosives
Arnhem, Natuurk	Natuurkunde. Tijdschrift, inhoudende Phijsica, Chemie, Pharmacie, Natuurlijke Historie en Litteratuur, uitgegeven van wege het Genootschap <i>Tot nut en vergenoegen</i> , te Arnhem
Arras, Mem Acad	Memoires de l'Academie d'Arras
Arras, Mem Soc Roy	Memoires de la Societe Royale d'Arras
Art J	The Art Journal
Artiz	The Artizan (London)
Artus, Jahr okon Chemie	Jahrbuch fur okonomische Chemie, etc
Artus, Vierteljahresschrift	Vierteljahresschrift fur technische Chemie, Landwirthschaftliche Gewerbe, Fabrickwesen und Gewerbetreibende uberhaupt
Ashmol Soc Proc	Abstracts of the Proceedings of the Ashmolean Society
Asiat Researches	Asiatic Researches, or Transactions of the (Bengal) Society
Asiat Soc J	Journal of the Royal Asiatic Society
Assoc Franc Compt rend	Association Francaise pour l'avancement des Sciences. Comptes Rendus
Assoc Med J	See Med Assoc Journ.
Assur Mag	The Assurance Magazine (and Journal of the Institute of Actuaries)
Astron Nachr	Astronomische Nachrichten
Astron Soc Mem	Memoirs of the Astronomical Society of London
Astron Soc Month Not	Monthly Notices of the Astronomical Society of London
Astrophys J	Astrophysical Journal
Atelier Phot	Atelier des Photographen
Ateneo Ital	L'Ateneo Italiano
Athenes Obs Nat Ann	Annales de l'Observatoire National d'Athenes
Atlantis	The Atlantis, or Register of Literature and Science
Atti Accad Ital	Atti dell'Accademia Italiana di Scienze
Atti accad Lincei	Atti della reale accademia dei Lincei, rendiconti, classe di scienze fisiche, matematiche e naturali
Atti Coll Ing Archit	Atti de Collegio degli Ingegneri ed Architetti in Milano
Atti inst incoragg	Atti del R istituto d'incoraggiamento di Napoli, Naples, Italy
Atti R Accad Sci Torino	Atti della Reale Accademia della Scienze di Torino
Atti Sci Ital	Riunione degli Scienziati Italiani
Atti Soc Elvet	Atti della Societa Elvetica delle Scienze Naturali
Aube, Mem Soc Agric	Memoires de la Societe d'Agriculture, des Sciences, et des Lettres du department de l'Aube
Augsb. Naturhist Ver Ber	Berichte des Naturhistorischen Vereins in Augsburg
Auk	The Auk A Quarterly Journal of Ornithology
Ausland	Das Ausland
Aust. P	Austrian Patent
Aust-Hung P	Austro-Hungarian Patent
Australasian Assoc Rep	Report of the Meeting of the Australasian Association for the Advancement of Science
Australasian J Pharm	Australasian Journal of Pharmacy, Melbourne
Australian Med. J.	Australian Medical Journal

Australia Med. Rec.	Medical Records of Australia
Australian P.	Australian P.
Australian Sugar J.	Australian Sugar Journal
Autun, Mem. Soc. Eduenne	Memoires de la Societe Eduenne
Auvergne, Ann. Sci.	Annales Scientifiques, Litteraires, et Industrielles de l'Auvergne
Auxerre, Bull. Soc. Sci.	Bulletin de la Societe des Sciences Historiques et Naturelles de l'Yonne
Badischen Aerzt. Verein. Mitth.	Mittheilungen des Badischen arztlichen Vereins
Bah. P.	Bahamas Patent
Ballenstedt, Archiv	Archiv fur die neuesten Entdeckungen aus der Urwelt
Ballot, Mag. Landbouw	Magazin voor Landbouw en Kruidkunde
Baltimore Med. Phys. Recorder	Baltimore Medical and Physical Recorder
Bamb. Naturf. Ges. Ber.	Bericht der naturforschenden Gesellschaft zu Bamberg
Barb. P.	Barbados Patent
Barcelona Acad. Bol.	Boletin de la Real Academia de Ciencias y Artes de Barcelona
Barcelona Acad. Mem.	Memorias de la Real Academia de Ciencias Naturales y Artes de Barcelona
Barrow Field Club Report	Barrow Naturalists' Field Club and Literary and Scientific Association. Annual Report and Proceedings
Basel, Ber.	Bericht uber die Verhandlungen der Naturforschenden Gesellschaft in Basel
Batavia Genootsch. Verh.	Verhandlungen van het Bataviaasch Genootschap der Kunsten en Wetenschappen
Batavia, Natuur. Archief.	Natuur- en Geneeskundig Archief voor Nederlandsch-Indie
Batavia, Natuurk. Tijdschr.	Natuurkundig Tijdschrift voor Nederlandsch-Indië, uitgegeven door de Koninklijke Natuurkundige Vereeniging in Nederlandsch-Indië
Batavia, Notulen	Notulen van de Algemeene en Bestuurs-Vergaderingen van het Bataviaasch Genootschap van Kunsten en Wetenschappen
Batavia Obs. Obsns.	Observations made at the (Royal) Magnetical and Meteorological Observatory at Batavia
Batavia, Tijdschr.	Tijdschrift voor Indische Taal-, Land-, en Volkenkunde
Batavia, Verh. Natuurk. Vereen.	Verhandlungen der Natuurkundige Vereeniging in Nederlandsch-Indië
Bath Micro. Soc. Minutes	Extracts from the Minutes of the Bath Microscopical Society
Bath Natur. Hist. Club. Proc.	Proceedings of the Bath Natural History and Antiquarian Field Club
Bath Soc. Agric. Letters	Letters and Papers of the Bath and West of England Society for the Encouragement of Agriculture, Arts, Manufactures, and Commerce
Baugew. Ztg.	Baugewerks-Zeitung
Baumgartner Zts.	Zeitschrift fur Physik, Mathematik, und verwandte Wissenschaften
Bayer. Gewerbeztg.	Bayerische Gewerbezeitung
Bayer. Kunst. Gewerbebl.	Kunst und Gewerbeblatt (Poletechn. Verein Konigreich Bayern)
Bayer, Landw. Ver. Erg.	Ergebnisse landwirtschaftlicher und agrikulturchemischer Versuche an der Station des General-Comite des Bayerischen Landwirthschaftlichen Vereines in Munchen

Bayeux, Mem. Soc. Agric.	Memoires de la Societe d'Agriculture, Sciences, Arts, et Belles-Lettres de Bayeux
Bd Trade J.	Board of Trade Journal
Beauvais, Soc Acad Mem.	Memoires de la Societe Academique d'Archeologie, Sciences et Arts du Department de l'Oise
Beitr. Anat. Physiol	See Eckhard
Beitr. Anthropol. Bayerns	Beitrage zur Anthropologie und Urgeschichte Bayerns. Organ der Munchener Gesellschaft für Anthropologie, Ethnologie und Urgeschichte
Beitr. Biol. Pflanz.	Beitrage zur Biologie der Pflanzen
Beitr. Geophys.	Beitrage zur Geophysik. Abhandlungen aus dem Geographischen Seminar der Universität Strassburg. Beitrage zur Geophysik Zeitschrift für Physikalische Erdkunde
Beitr. Kryptog. Schweiz	Beitrage zur Kryptogamenflora der Schweiz
Beitr. Mecklenb. Aerzte	Beitrage Mecklenburgischer Aerzte zur Medicin und Chirurgie
Beitr. Morphol.	Beitrage zur Morphologie und Morphogenie Untersuchungen aus dem Anatomischen Institut zu Erlangen
Beitr. Naturk. Preussens	Beitrage zur Naturkunde Preussens Herausgegeben von der Königl. Physikalisch-Oekonomischen Gesellschaft zu Königsberg
Beitr. Palaont. Oesterr.-Ung.	Beitrage zur Palaontologie Oesterreich-Ungarns und des Orients
Beitr. Path. Anat.	Beitrage zur Pathologischen Anatomie und Physiologie Beitrage zur Pathologischen Anatomie und zur Allgemeinen Pathologie
Beitr. Physiol. Morphol.	Beitrage zur Physiologie und Morphologie Niedriger Organismen
Beitr. Russ. Reich.	Beitrage zur Kenntniss des Russischen Reiches und der angrenzenden Länder Asiens
Belfast, Clin. Soc. Trans.	Transactions of the Clinical and Pathological Society of Belfast
Belfast Field Club Rep.	Annual Reports and Proceedings of the Belfast Naturalists' Field Club
Belfast Natur. Hist. Soc. Proc.	Proceedings of the Belfast Natural History and Philosophical Society
Belg. Horticole	La Belgique Horticole Annales de Botanique et d'Horticulture
Belg. P.	Belgian Patent
Bengal Asiat. Soc. J.	Journal of the Asiatic Society of Bengal
Bengal Asiat. Soc. Proc.	Proceedings of the Asiatic Society of Bengal
Bengal Govt. Records	Selections from the Records of the Bengal Government
Bengal, Phot. Soc. J. Ber.	Journal of the Photographic Society of Bengal Berichte der Deutschen Chemischen Gesellschaft, Berlin
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft
Ber. pharm. Ges.	Berichte der deutschen pharmazeutischen Gesellschaft
Ber. phys. Ges.	Berichte der deutschen physikalischen Gesellschaft
Ber. Sachs. Ges. Wiss.	Berichte über die Verhandlungen der Königl. Sachs. Gesellschaft der Wissenschaften zu Leipzig
Ber. Veter. König. Sach.	Berichte über das Veterinärwesen im Königreich Sachsen
Berg. Hüttenm. Jahr.	Berg- und hüttenmannisches Jahrbuch
Berg. Hüttenm. Ztg.	Berg- und hüttenmannische Zeitung

Bergens Mus. Aarb.	Bergens Museums Aarbog for... Afhandlinger og Aarsberetning udgivne af Bergens Museum
Berggeist	Der Berggeist
Berghaus, Ann.	Annalen der Erd-, Volker- und Staatenkunde
Berghaus, Zts. Erdk	Zeitschrift für vergleichende Erdkunde
Berlin Afrik. Ges. Mitth.	Mittheilungen der Afrikanischen Gesellschaft in Deutschland
Berlin Akad. Abh.	Abhandlungen der k. Akademie der Wissenschaften zu Berlin
Berlin Akad. Monatsber.	Monatsberichte der k. Preussischen Akademie der Wissenschaften zu Berlin
Berlin Akad. Sitzber.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin
Berlin Ann. Telegr.	Annalen der Telegraphie
Berlin Astron. Jahr.	Berliner Astronomisches Jahrbuch
Berlin Bot. Gartens Jahr	Jahrbuch des Königl. Botanischen Gartens und des Botanischen Museums zu Berlin
Berlin Bot. Gartens Notizbl.	Notizblatt des Königl. Botanischen Gartens und Museums zu Berlin
Berlin Ent. Ges.	See III Wschr Ent
Berlin Entom. Zts.	Berliner Entomologische Zeitschrift, herausg. von dem Entomologischen Verein in Berlin
Berlin Ges. Anthropol. Verh.	See Ztschr. Ethnol
Berlin Ges. Erdk. Verh.	Verhandlungen der Gesellschaft für Erdkunde zu Berlin
Berlin Ges. Erdk. Zts.	See Berlin Zts. Erdk
Berlin Ges. Geburtshlf. Gynak.	See Zts. Geburtshlf. Gynak.
Berlin Ges. Naturf. Freunde Mag.	Magazin der Gesellschaft Naturforschender Freunde zu Berlin, für die neuesten Entdeckungen in der gesammten Naturkunde
Berlin Ges. Naturf. Freunde N. Schr.	Neue Schriften der Gesellschaft Naturforschender Freunde in Berlin
Berlin Ges. Naturf. Freunde Verh.	Verhandlungen der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Ges. Psychiatr.	See Arch. Psychiatr.
Berlin Gesundheitsamt Biol. Abth. Arb.	Arbeiten aus der Biologischen Abtheilung für Land- und Forstwirtschaft am Kaiserlichen Gesundheitsamte
Berlin Ind. Ztg.	Industrie Zeitung, Berlin
Berlin Jahr. Pharm.	Berlinisches Jahrbuch für die Pharmacie und für die damit verbundenen Wissenschaften
Berlin Klin. Wochenschr.	Berliner klinische Wochenschrift
Berlin Mem. Acad.	Memoires de l'Academie Royale des Sciences de Berlin
Berlin Mitth. Ges. Naturf.	Mittheilungen aus den Verhandlungen der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Monatsber.	Monatsberichte der K. Preuss. Akademie der Wissenschaften zu Berlin
Berlin Monatsber. Ges. Erdk.	Monatsberichte über die Verhandlungen der Gesellschaft für Erdkunde zu Berlin
Berlin Naturf. Freunde Sitzber.	Sitzungs-Berichte der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Neue Zts. Geburtsk.	Neue Zeitschrift für Geburtskunde
Berlin Physiol. Ges. Verh.	See Arch. Anat. Physiol
Berlin Physik. Reichsanst. Abh.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt
Berlin Verh. Med. Ges.	Verhandlungen der Berliner medicinischen Gesellschaft

Berlin Zool. Mus. Mitth.	Mittheilungen aus der Zoologischen Sammlung des Museums für Naturkunde in Berlin
Berlin Zts. Erdk.	Zeitschrift der Gesellschaft für Erdkunde zu Berlin
Berlin Mitth.	Mittheilungen der Naturforschenden Gesellschaft in Bern
Berwick, Natur. Club Hist.	History of the Berwickshire Naturalists' Club
Berz. Jahr. Chem.	Berzelius Jahresberichte der Chemie
Besancon, Mem. Soc. Emul.	Memoires et Comptes Rendus de la Societe (Libre) d'Émulation du Doubs
Besancon, Seances Publ	Seances publiques de l'Academie des Sciences, Arts, et Belles-Lettres de Besancon
Beton Eisen	Beton und Eisen
Betterave	Betterave
Beziers Soc. Sci. Bull	Bulletin de la Société d'Étude des Sciences Naturelles de Beziers
Bianconi, Rep Ital.	Repertorio Italiano Per la Storia Naturale
Bibl Anat.	Bibliographie Anatomique. Revue des Travaux en langue française Anatomie. Histologie Embryologie. Anthropologie
Bibl Bot.	Bibliotheca Botanica Abhandlungen aus dem Gesamtgebiete der Botanik
Bibl Brit.	Bibliothèque Britannique, ou Recueil extrait des Ouvrages Anglais periodiques et autres, partie des Sciences et Arts
Bibl Ital	Giornale dell' I. R. Istituto Lomgardo di Scienze, Lettere ed Arti, e <i>Biblioteca Italiana</i>
Bibl Math.	Bibliotheca Mathematica. Zeitschrift für Geschichte der Mathematik Journal d'Histoire des Mathematiques Bibliotheca Mathematica. Zeitschrift für Geschichte der mathematischen Wissenschaften
Bibl Univ	Bibliothèque Universelle des Sciences, Archives des Sciences Physiques et Naturelles
Bibl Zool.	Bibliotheca Zoologica
Bied Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb
Bierbrauer	Der Bierbrauer
Bjdr tot de Dierkunde	Bijdragen tot de Dierkunde
Biochem. Bull.	Biochemical Bulletin
Biochem. J.	The Bio-Chemical Journal
Biochem. Zentr	Biochemisches Zentralblatt, Leipzig
Biochem. Zts.	Biochemische Zeitschrift
Biol. Bull.	Biological Bulletin
Biol. Zentr.	Biologisches Zentralblatt
Biophys. Zentr.	Biophysikalisches Zentralblatt, Leipzig
Birmingham Natur. Hist & Micro. Soc. Trans.	See Midland Natlist Trans
Birmingham Phil Soc Proc	Proceedings of the Birmingham Philosophical Society
Blankenburg, Ber.	Berichte des Naturwissenschaftlichen Vereins des Harzes zu Blankenburg
Blatter Blech-Arb.	Deutsche Blätter für Blecharbeiter
Blätter Kunstgew.	Blätter für Kunstgewerbe
Blätter Zuckerrub	Blätter für Zuckerrubenbau
Bleekrode, Nieuw Tijdschrift	Nieuw Tijdschrift gewijd aan alle takken van Volkswijst, Nijverheid, Landbouw, Mijnwezen, Handel, Spoorwegen, Telegraphie en Scheepvaart
Blois, Mem Soc. Sci.	Memoires de la Société des Sciences et des Lettres de Blois
Blois, Soc. Loir et Cher Mem.	Memoires de la Société des Sciences et Lettres de Loir et Cher

Boerhaave	Boerhaave
Böhm. Ges. Abh.	Abhandlungen der Königlich Böhmischen Gesellschaft der Wissenschaften
Böhm. Ges. Wiss. Jahr.	Jahresbericht der königl. böhm. Gesellschaft der Wissenschaften
Bohm. Monatschr. Ges. Mus.	Monatschrift des Gesellschaft des Vaterländischen Museums in Böhmen
Bol. P.	Bolivia Patent
Boll. chim. farm.	Bolletino chimico farmaceutico, Milan
Boll. estac. agr. Ciudad Juarez	Boletin de la estacion agricola experimental de Ciudad Juarez
Boll. ingen.	Boletin de ingenieros
Boll. Natur. Siena	Bollettino del Naturalista Collettore, Allevatore, Coltivatore
Bologna Accad. Sci. Mem	Memorie della (R.) Accademi delle Scienze dell' Istituto di Bologna
Bologna, Mem. Inst. Naz. Ital.	Memorie dell'Istituto Nazionale Italiano
Bologna, Mem. Soc. Med.	Memorie della Societa Medica di Bologna
Bologna, Mem. Soc. Med. Chir.	Memorie della Societa Medico-chirurgica di Bologna
Bologna, Nov. Comment.	Novi Commentarii Academiae Scientiarum Instituti Bononiensis
Bologna, Opusc.	Opuscoli della Societa Medico-chirurgica di Bologna
Bologna, Opusc. Sci.	Opuscoli Scientifici
Bologna, Opusc. Sci. N. Coll	Nuova collezione d'Opuscoli Scientifici
Bologna Rend.	Rendiconto delle Sessioni dell' Accademia Reale delle Scienze dell' Istituto di Bologna
Bombay, Agric. Hort. Soc. Proc.	Proceedings of the Agricultural and Horticultural Society of Western India
Bombay Govt. Records	Selections from the Records of the Bombay Government
Bombay, Med. Phys. Soc. Trans.	Transactions of the Medical and Physical Society of Bombay
Bombay Natur. Hist. Soc. J.	The Journal of the Bombay Natural History Society
Bombay, Roy. Asiat. Soc. J.	The Journal of the Bombay Branch of the Royal Asiatic Society
Bone, Acad. Hippone Bull.	Bulletin de l'Academie d'Hippone
Bonn, Corresp. Blatt Nat. Hist. Ver.	Correspondenzblatt des Naturhistorischen Vereins für Rheinland und Westphalen
Bonn, Niederrhein. Ges. Sitzber.	Sitzungsberichte der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn
Bonn, Untersuch. Physiol. Lab.	Untersuchungen aus dem physiologischen Laboratorium zu Bonn
Bonn, Verh. Naturhist. Ver.	Verhandlungen des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Bonplandia	Bonplandia
Bordeaux, Acad. Sci. Seances Publ.	Seances publiques de l'Academie Royale des Sciences, Belles-Lettres, et Arts de Bordeaux
Bordeaux, Actes Acad. Sci	Recueil des Actes de l'Academie des Sciences, Belles-Lettres, et Arts de Bordeaux
Bordeaux, J. Med.	Journal de Medecine de Bordeaux
Bordeaux, J. Med. Prat.	Journal de Medecine pratique, ou Recueil des Travaux de la Société de Medecine de Bordeaux
Bordeaux, Mem. Soc. Med. Chir.	Memoires et Bulletins de la Société Medico-Chirurgicale des Hopitaux et Hospices de Bordeaux
Bordeaux, Mem. Soc. Sci. Phys.	Memoires de la Société des Sciences Physiques et Naturelles de Bordeaux

Bordeaux, Soc Linn Actes	Actes de la Société Linneenne de Bordeaux
Bordeaux, Soc Linn Bull	Bulletin d'Histoire Naturelle de la Société Linneenne Bordeaux
Bordeaux, Soc Med Mem	Memoires et Bulletins de la Société de Medecine et de Chirurgie de Bordeaux
Bordeaux, Soc Sci P-V	Proces-Verbaux des Seances de la Société des Sciences Physiques et Naturelles de Bordeaux
Bornemann, Der Ingenieur	Der Ingenieur
Boston J Phil	The Boston Journal of Philosophy and the Arts
Boston J Natur Hist	Boston Journal of Natural History
Boston Med Surg. J	Boston Medical and Surgical Journal
Boston, Mem Amer Acad	Memoirs of the American Academy of Arts and Sciences
Boston, Mem Natur Hist Soc	Memoirs read before the Boston Society of Natural History
Boston Pap. Soc. Natur Hist.	Occasional papers of the Boston Society of Natural History
Boston, Proc Natur. Hist Soc	Proceedings of the Boston Society of Natural History
Boston Soc Med Sci J.	Journal of the Boston Society of Medical Sciences
Bot Centr.	Botanisches Centralblatt Referirendes Organ für das Gesamtgebiet der Botanik des In- und Auslandes
Bot Centr Beihefte	Beihefte zum Botanischen Centralblatt
Bot Cong Proc.	The International Horticultural Exhibition and Botanical Congress Report of Proceedings
Bot Gaz	The Botanical Gazette
Bot Jahr. (Engler)	Botanische Jahrbücher, Engler, Leipzig
Bot Mag, Tokyo	The Botanical Magazine, Tokyo
Bot. Notiser	Botaniska Notiser
Bot Tidsskr	Botanisk Tidsskrift udgivet af den Botaniske Forening i Kjobenhavn
Bot Untersuch	Botanische Untersuchungen aus dem Physiologischen Laboratorium der landwirthschaftlichen Lehranstalt in Berlin
Bot Untersuch (Brefeld's)	Untersuchungen aus dem Gesamtgebiete der Mykologie
Bot Ver Gesamtthuringen	See Jena Geogr Ges Mitth.
Botan. Ztg.	Botanische Zeitung
Bot Zentr.	Botanisches Zentralblatt
Botaniste	Le Botaniste
Bouchardat, Archiv.	Archives de Physiologie, de Therapeutique, et d'Hygiene
Boue, J. Geol.	Journal de Geologie
Boulogne, Mem Soc Agric	Memoires de la Société d'Agriculture, etc, de Boulogne-sur-Mer
Bourse cuirs Liege	Bourse aux cuirs de Liege, bulletin hebdomadaire
Brandenb Bot Ver. Verh	Verhandlungen des botanischen Vereins für die Provinz Brandenburg
Brass World	Brass World and Platers Guide, The
Braunk	Braunkohle
Braunschw. Ver Naturwiss Jahr.	Jahresbericht des Vereins für Naturwissenschaft zu Braunschweig
Braz. P.	Brazilian Patent
Bremen Abh.	Abhandlungen herausgegeben vom Naturwissenschaft- lichen Verein zu Bremen
Brenn. Ztg.	Brennerei Zeitung
Brera, Giorn Med. Prat.	Giornale di Medicina Pratica
Brera, Nuovi Comment.	Nuovi Commentari di Medicina

Brescia, Comment Ateneo	Commentarj della Accademia di Scienze, Lettere, ed dell'Ateneo di Brescia
Breslau, Ann Klin. Inst	Annalen des Klinisch-chirurgischen Instituts auf der Universität zu Breslau
Breslau, Bot. Garten Arb.	Arbeiten aus dem Königl. Botanischen Garten zu Breslau
Breslau, Gewerbebl.	Breslauer Gewerbeblatt
Breslau, Jahr. Schles. Ver. Berg.	Jahrbuch des Schlesischen Vereins für Berg- und Huttenwesen
Breslau, Schles. Ges. Jahr.	Jahresbericht des Akademischen Naturwissenschaftlichen Vereins zu Breslau
Breslau, Studien. Physiol. Inst.	Studien des Physiologischen Instituts zu Breslau
Breslau, Zts. Klin. Med.	Zeitschrift für Klinische Medizin
Brest Soc. Acad. Bull.	Bulletin de la Société Académique de Brest
Brewers J. (Lon.)	Brewers Journal and Hop and Malt Trades Review, The (London)
Brewers J., N. Y.	Brewers Journal, New York
Brick	Brick
Brick J.	Brick, Pottery and Glass Journal
Brick and Clay Record	Brick and Clay Record
Brighton, Proc. Natur. Hist. Soc.	Reports and Abstracts of the Proceedings of the Brighton and Sussex Natural History Society
Bristol Proc. Nat. Soc.	Proceedings of the Bristol Naturalists' Society
Brit. Assoc. Rep.	Report of the Meetings of the British Association for the Advancement of Science
Brit. Clay Worker	British Clay Worker, The
Brit. Food J.	British Food Journal
Brit. For. Med. Chir. Rev.	British and foreign Medico-Chirurgical Review
Brit. Inst. Publ. Health	See J. State Med.
Brit. J. Almanac	British Journal of Photography Almanac
British J. Dent. Sci.	The British Journal of Dental Science
Brit. J. Phot.	British Journal of Photography
Brit. Med. J.	British Medical Journal
Brit. Mycol. Soc. Trans.	The British Mycological Society Transactions
Brit. Pharm. Confer. Proc.	Proceedings of the British Pharmaceutical Conference
Brit. Pharm. Confer. Trans.	Year Book of Pharmacy, comprising Abstracts of Papers With the Transactions of the British Pharmaceutical Conference
Brit. Colon. Drug	British and Colonial Druggist, London
Brit. Guiana Agr. Soc.	See Timehri
Brit. Guiana P.	British Guiana Patent
Brit. Hond. P.	British Honduras Patent
Brooklyn Entom. Soc. Bull.	Bulletin of the Brooklyn Entomological Society
Brosche, Zts.	Zeitschrift für Natur- und Heilkunde
Broussais, Ann.	Annales de la Médecine Physiologique
Brown-Sequard, J. Physiol.	Journal de la Physiologie de l'Homme et des Animaux
Brugnatelli, Giorn.	Giornale di Fisica, Chimica, e Storia Naturale
Brunn Verh.	Verhandlungen des Naturforschenden Vereines in Brunn
Brux Acad. Bull.	Bulletins de l'Académie Royale des Sciences, etc., de Belgique
Brux Acad. Cent. Anniv.	Centième Anniversaire de Fondation de l'Académie Royale de Belgique
Brux Acad. Med. Belg. Bull.	Bulletin de l'Académie Royale de Médecine Belgique
Brux Acad. Sci. Mem.	Nouveaux mémoires de l'Académie Royale, des Sciences et Belles-lettres de Bruxelles



Brux Actes Soc. Med.	Actes de la Société Médicale de Bruxelles
Brux. Ann. Soc. Entom. Belge	Annales de la Société Entomologique Belge
Brux Ann. Soc. Malacol.	Annales de la Société Malacologique de Belgique
Brux. Ann. Trav. Pub.	Annales des Travaux Publics de Belgique
Brux Ann. Univ. Belg.	Annales des Universités de Belgique
Brux Bull. Belge Phot.	Bulletin Belge de la Photographie
Brux Bull. Soc. Bot.	Bulletins de la Société Royale de Botanique de Belgique
Brux Congr. Bot. Act.	Actes du Congrès de Botanique horticole réunis à Bruxelles
Brux Congr. Bot. (C. R.)	Congrès de Botanique et d'Horticulture de 1880 tenu à Bruxelles
Brux. J. Med.	Journal de Médecine, de Chirurgie, et de Pharmacologie
Brux. J. Soc. Centr. Agric.	Journal de la Société Centrale d'Agriculture de Belgique
Brux Mem. Couronn.	Mémoires Couronnés et Mémoires des Savants Étrangers
Brux. Mus. Congo Ann.	État Indépendant du Congo. Annales du Musée du Congo, publiées par ordre du Secrétaire d'État
Brux. Mus. Hist. Natur. Ann.	Annales du Musée Royal d'Histoire Naturelle de Belgique
Brux. Mus. Hist. Natur. Bull.	Bulletin du Musée Royal d'Histoire Naturelle de Belgique
Brux. Mus. Hist. Natur. Mem.	Mémoires du Musée Royal d'Histoire Naturelle de Belgique
Brux. Soc. Agric. Journ.	Journal de la Société Centrale d'Agriculture de Belgique
Brux. Soc. Belge Micro Ann.	Annales de la Société Belge de Microscopie
Brux. Soc. Belge Micro Bull.	Bulletin (des Séances) de la Société Belge de Microscopie
Brux. Soc. Entom. Ann.	Annales de la Société Entomologique de Belgique
Brux. Soc. Entom. Mem.	Mémoires de la Société Entomologique de Belgique
Brux. Soc. Linn. Bull.	Bulletin de la Société Linéenne de Bruxelles
Brux. Soc. Sci.	See Rev. Quest. Sci.
Brux. Soc. Sci. Ann.	Annales de la Société Scientifique de Bruxelles
Bucarest. Acad. Rom. Anal.	Analele Academiei Române
Bucarest Soc. Sci. Bul.	Buletinul Societății de Științe (Fizică, Chimie, și Mineralogie) din București-România. Bulletin de la Société des Sciences, Bucarest-Roumanie
Buchholz	See Annab.-Buchh. Ver. Nat. Jber.
Buda, Evkönyvei	A' Magyar Tudós Társaság' Evkönyvei (Year Books of the Hungarian Scientific Association)
Buda, Pályamunkák.	Természettudományi Pályamunkák
Buda, Tudománytar.	Tudománytar Közre bocsátja a' Magyar Tudós Társaság
Buffalo Bull.	Bulletin of the Buffalo Society of Natural Sciences
Builder	The Builder
Buitenzorg Inst. Bot. Bull.	's Lands Plantentuin. Bulletin de l'Institut Botanique de Buitenzorg
Buitenzorg Jard. Bot. Ann.	Annales du Jardin Botanique de Buitenzorg
Bull. Acad. Med.	Bulletin of the Academy of Medicine
Bull. Acad. roy. Belg.	Académie royale de Belgique, Bulletin de la Classe des Sciences
Bull. Acad. Sci., Cracow.	Bulletin international de l'Académie des Sciences de Cracovie

Bull. Acad. Sci., Petrograd	Bulletin de l'Academie Imperiale des Sciences de Petrograd
Bull Amer. Inst. Min. Eng	Bulletin American Institute of Mining Engineers
Bull Amer. Pharm. Assoc	Bulletin of the American Pharmaceutical Association
Bull. assoc. chim. suc. dist	Bulletin de l'association des chemists de sucrerie distillerie de France
Bull Bur. Agric	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases
Bull Bur Chem U. S. Dept. Agric.	Bulletins, Bureau of Chemistry, U. S Department of Agriculture
Bull. Bur. Mines	Bureau of Mines Bulletin, Department of the Interior
Bull. Bur Standards	Bulletin of the Bureau of Standards
Bull. Col. School Mines	Bulletin of the Colorado School of Mines
Bull Dept. Agric Jamaica	Bulletin of the Department of Agriculture, Jamaica
Bull. Dept Agric Trinidad	Bulletin of Agricultural Information, Department of Agriculture, Trinidad
Bull Geol. Inst. Univ. Upsala	Bulletin of the Geological Institute of the University of Upsala
Bull Geol Soc. Amer.	Bulletin of the Geological Society of America
Bull Hyg Lab.	Bulletins of the Hygienic Laboratory, United States Public Health and Marine Hospital Service
Bull Imp Inst.	Bulletin of the Imperial Institute, London
Bull Iron Assoc.	Bulletin of the American Iron and Steel Association
Bull Johns Hopkins Hosp.	Bulletin of Johns Hopkins Hospital
Bull Mass Inst. Tech.	Bulletin of the Massachusetts Institute of Technology
Bull Med Belge	Bulletin Medical Belge.
Bull Musee	Bulletin du Musee de l'industrielle de Belgique
Bull Pharmacie	Bulletin de Pharmacie
Bull. Pharmacy	Bulletin of Pharmacy
Bull Pharm Sud-est	Bulletin de Pharmacie du Sud-est, Montpellier
Bull Sci France Belg.	Bulletin Scientifique de la France et de la Belgique
Bull Sci Nord	Bulletin Scientifique, Historique et Litteraire du Department du Nord et des pays voisins
Bull Sci pharmacolog.	Bulletin des Sciences pharmacologiques
Bull Soc Bot. France	Bulletin de la Société Botanique de France
Bull Soc Bot Belg.	Bulletin de la Société Royale de Botanique de Belgique
Bull Soc Chim.	Bulletin de la Société Chimique de France
Bull Soc Chim Belg.	Bulletin de la Société Chimique de Belgique
Bull Soc Encourag	Bulletin de la Société d'Encouragement
Bull Soc franc Mineral	Bulletin de la Société Francaise de Mineralogie
Bull Soc franc Phot.	Bulletin de la Société Francaise de Photographie
Bull Soc geol France	Bulletin de la Société geologique de France
Bull Soc. Ind. Amiens	Bulletin de la société industrielle d'Amiens
Bull. Soc. Ind Marseille	Bulletin de la Société industrielle de Marseille
Bull Soc. Ind Minerale	Bulletin de la société de l'industrie minerale
Bull Soc Ind. Mulh.	Bulletin de la société industrielle de Mulhouse
Bull. Soc. Ind Nord	Bulletin mensuel de la société industrielle du Nord
Bull Soc. Ind Rouen	Bulletin de la société industrielle de Rouen
Bull. Soc internat elect	Bulletin de la Société internationale des electriciens
Bull. Soc. Med Amiens	Bulletin des Travaux de la Société Medicale d'Amiens
Bull. Soc. med Gand	Bulletin de la Société de Medecine de Gand
Bull Soc. Mycol	Bulletin de la Société Mycologique de France
Bull Soc. pharm Bord	Bulletin de la société pharmacie de Bordeaux
Bull Soc phot. Belg.	Bulletin de la Société photographique de Belgique
Bull Soc. Romane Stiin	Buletinul societatii Romane de Stiinte
Bull. Soc. roy pharm.	Bulletin de la société de pharmacie de Bruxelles royale
Bull. Soc sci med. Rennes	Bulletin de la société scientifique et medicale de l'ouest, Rennes

Bull. Soc. vaudoise	Bulletin de la Société vaudoise des Ingenieurs et des Architects
Bull. Torrey Bot. Club	Bulletin of the Torrey Botanical Club, New York
Bull. Vulc. Ital.	Bullettino del Vulcanismo Italiano (e di Geodinamica generale)
C. A.	Chemical Abstracts
Cabanis, J. Ornithol.	Journal für Ornithologie
Cadiz, Period. Mens. Cien	Periodico mensual de Ciencias matematicas y fisicas
Caen, Acad. Mem.	Memoires de l'Academie des Sciences, Belles Lettres, et Arts de Caen
Caen, Bull. Soc. Linn. Normandie	Bulletin de la Société Linneene de Normandie
Caen, Mem. Soc. Linn. Normandie	Memoires de la Société Linneenne de Normandie
Caen, Travaux	Precis des Travaux de la Société d'Agriculture, &c de Caen
Calcutta, J. Natur. Hist.	The Calcutta Journal of Natural History
Calcutta, Quart. J.	Quarterly Journal of the Medico-Physical Society
Calcutta Roy. Bot. Gard. Ann.	Annals of the Royal Botanic Garden, Calcutta
Calcutta, Trans. Med. Phys. Soc.	Transactions of the Medical and Physical Society of Calcutta
Cal. Acad. Bull.	Bulletin of the California Academy of Sciences
Cal. Acad. Mem.	Memoirs of the California Academy of Sciences
Cal. Acad. Natur. Sci. Proc.	Proceedings of the Californian Academy of Natural Sciences
Cal. Acad. Pap.	Occasional Papers of the California Academy of Sciences
Cal. Min. Bur. Bull.	California State Mining Bureau Bulletin
Cal. Min. Bur. Rep.	(California State Mining Bureau) Report of the State Mineralogist
Calvados, Mem. Soc. Linn.	Memoires de la Société Linneenne du Calvados
Cambrai, Mem. Soc. Emul.	Memoires de la Société d'Emulation de Cambrai
Cambridge Mem. Analyt. Soc.	Memoirs of the Cambridge Analytical Society
Cambridge Mus. Comp. Zool. Bull.	Proceedings of the Museum of Comparative Zoology at Harvard College, Cambridge, Mass
Cambr. Ornith. Club Bull.	Bulletin of the Nuttall Ornithological Club. A Quarterly Journal of Ornithology
Cambridge Phil. Soc. Proc.	Proceedings of the Cambridge Philosophical Society
Cambridge Phil. Soc. Trans.	Transactions of the Cambridge Philosophical Society
Cambridge, Studies Physiol. Labor.	Studies from the Physiological Laboratory in the University of Cambridge
Camera Oscura	La Camera Oscura, rivista periodica universale dei progressi della Fotografia
Can.	Canadian—Canada
Can. Bot. Soc. Ann.	Annals of the Botanical Society of Canada
Can. Chem. J.	The Canadian Chemical Journal
Can. Drug.	Canadian Druggist
Can. Eng.	Canadian Engineer, The
Can. Entom.	The Canadian Entomologist
Can. Entom. Soc. Rep.	First Annual Report on the Noxious Insects of the Province of Ontario
Can. Inst. Proc.	Proceedings of the Canadian Institute (Toronto, being a continuation of "The Canadian Journal of Science, Literature and History")
Can. Inst. Trans.	Transactions of the Canadian Institute
Can. J.	The Canadian Journal of Industry, Science, and Art

Can Naturalist	The Canadian Naturalist and Geologist, and Proceedings of the Natural History Society of Montreal
Can P.	Canadian Patent
Can Pat Off Rec	Canadian Patent Office Record
Can Pharin J	Canadian Pharmaceutical Journal and Pharmacal Gazette
Can Rec Sci	The Canadian Record of Science, including the Proceedings of the Natural History Society of Montreal, and replacing the Canadian Naturalist
Can Roy Soc Proc Trans	Proceedings and Transactions of the Royal Society of Canada
Canestrini	See Archivio Zool
Canestrini, Archiv	Archivio per la Zoologia, l Anatomia, e la Fisiologia
Cannes Soc Mem	Memoires de la Société des Sciences Naturelles (et Historiques), des Lettres et des Beaux-Arts de Cannes, et de l'arrondissement de Grasse
Cantu, Cronaca	Cronaca
Caout Gutta p	Caoutchouc et la Gutta-percha
Caradoc Field Club Trans	Transactions of the Caradoc and Severn Valley Field Club
Cardiff Natur Soc Trans	Cardiff Naturalists' Society Report and Transactions
Carinthia	See Karnten
Carl, Rep Physik	Repertorium fur Experimental Physik, etc (Rep der Physik)
Carlsberg Lab	See under Kiobenh
Carlsruhe	See Karlsruhe
Carlsruhe, Verh Naturwiss Ver.	Verhandlungen des Naturwissenschaftlichen Vereins
Carloinisches Medicq-Chirurgisches Institut.	See under Stockh Physiol Lab Mitth
Carus, Zool Anzeiger	Zoologischer Anzeiger
Casopis	Casopis pro Pestovani Matematiky a Fysiky (Journal for the Advancement of Mathematics and Physica)
Casopis Cesketho Lekarn	Casopis Cesketho Lekarnitura
Casper Vierteljahrssch	Vierteljahrsschrift fur gerichtliche und öffentliche Medicin
Casper Wochensch	Wochenschrift fur die gesammte Heilkunde
Cassel Jahr	Jahresbericht, dann Bericht, über die Thatigkeit des Vereins fur Naturkunde in Cassel
Cassier s Mag.	Cassiers's Magazine
Castings	Castings
Catania Atti Accad Gioen	Atti dell'Accademia Gioenia di Scienze Naturali di Catania
Catania Boll Accad Gioen	Bollettino delle Sedute della Accademia Gioenia
Cattaneo Bibl di Farm	Biblioteca di Farmacia, Chimica, etc.
Cattaneo Giorn Farm.	Giornale di Farmacia
Cell. Ind.	Die Celluloid Industrie
Cellule	La cellule
Cement	Cement
Cement Age	Cement Age
Cement Eng News	Cement and Engineering News
Cement Record	Cement Record
Centr Agrik Chem.	Central-Blatt fur Agrikulturchemie und rationellen Wirtschafts-Betrieb Referirendes Organ fur naturwissenschaftliche Forschungen in ihrer Anwendung auf die Landwirtschaft
Centr Allg Path.	Centralblatt fur allgemeine Pathologie

Centr. Bakt.	Centralblatt für Bacteriologie und Parasitenkunde
Centr. Med. Wiss.	Centralblatt für die medicinischen Wissenschaften
Centr. Mineral	Centralblatt für Mineralogie, Geologie und Palaeontologie
Centr. Papierfabr	Centralblatt für Papierfabrikation
Centr. Path	Centralblatt für Allgemeine Pathologie und Pathologische Anatomie
Centr. Physiol	Centralblatt für Physiologie
Centr. Text. Ind	Centralblatt für die Textil-Industrie
Centr. Zuckerind	Centralblatt für die Zuckerindustrie
Centrztg. Optik	Central-Zeitung für Optik und Mechanik (Elektrotechnik und verwandte Berufszweige)
Ceramique	Ceramique, La
Cette Stat. Maritime	See Montpellier Inst. Zool. Trav.
Cey P.	Ceylon Patent
Chamb. Comm. J.	Chamber of Commerce Journal
Chambery Mem. Acad. Savoie.	Memoires de la Societe Academique de Savoie.
Charente-Inf. Soc. Sci. Ann.	Academie de la Rochelle. Societe des Sciences Naturelles de la Charente-Inferieure Annales
Charkoff.	See Kharkov
Charleston Med. Journ.	Charleston Medical Journal and Review
Charleston South J. Med.	The Southern Journal of Medicine
Chem. Age	Chemical Age
Chem. Centr.	Chemisches Centralblatt (1830-1906)
Chem. Coll. Reports	Reports of the Royal College of Chemistry, and Researches conducted in the Laboratories
Chem. Drug	Chemist and Druggist, London
Chem. Drug. Australasia	Chemist and Druggist of Australasia
Chem. Eng.	Chemical Engineer
Chem. Gaz.	Chemical Gazette, The
Chem. Ind.	Chemische Industrie
Chem. Listy	Chemické Listy
Chem. News	Chemical News
Chem. Pharm. Centr. Blatt.	Chemisch-pharmaceutisches Central-Blatt
Chem. Rev.	The Chemical Review
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett-und Harz-Industrie
Chem. Tech. Mitth.	Elsner's Chemisch-Technische Mittheilungen
Chem. Tech. Rep.	Chemisch-Technisches Repertorium (Jacobsen 1862-1901)
Chem. Tech. Neuzeit	Chemische Technologie der Neuzeit
Chem. Tech. Übers.	Chemisch-Technische Übersicht (supplement to Chem. Ztg.)
Chem. Tech. Ztg.	Chemiker-und Techniker-Zeitung
Chem. Trade J.	Chemical Trade Journal and Chemical Engineer
Chem. Weekbl.	Chemisch Weekblad
Chem. World	Chemical World, The
Chem. Zentr.	Chemisches Zentralblatt (1907-)
Chem. Ztg.	Chemiker-Zeitung
Chem. Ztg. Rep.	Repertorium der Chemiker Zeitung
Chem. Zts.	Chemische Zeitschrift
Chemist	The Chemist
Chemnitz Ber.	Bericht der Naturwissenschaftlichen Gesellschaft zu Chemnitz
Cherbourg, Acad. Mem. Soc.	Memoires de la Société Academique de Cherbourg
Cherbourg, Sci. Mem. Soc.	Memoires de la Société Imperiale des Sciences Naturelles de Cherbourg

Cherbourg Soc. Sci Natl Mem.	Memoires de la Société Nationale des Sciences Naturelles et Mathematiques de Cherbourg
Chester Soc Sci Proc.	Proceedings of the Chester Society of Natural Science (and Literature)
Chicago Acad Sci. Bull	Bulletin of the Chicago Academy of Sciences
Chicago Acad. Sci. Bull. Nat. Hist. Surv.	The Chicago Academy of Sciences. Bulletin.. of the Natural History Survey
Chicago Acad Sci Trans.	Transactions of the Chicago Academy of Sciences
Chicago Entom. Soc Mem	Occasional Memoirs of the Chicago Entomological Society
Chicago Field Columb. Mus. Publ.	Publications of the Field Columbian Museum
Chile, Anales Univ.	Anales de la Universidad de Chile
Chile P.	Chilean Patent
Chili Soc Sci Act.	Actes de la Société Scientifique du Chili (Actas de la Sociedad Cientifica de Chile)
Chim et Ind.	Chimie et Industrie
Chimiste	Chimiste, Le
Christiania, Forh	Forhandlinger i Videnskabs-Selskabet i Christiania
Christiania, Norsk Mag	Norsk Magazin for Laegevidenskaben
Christiania Skr. (Math. - Nat. Kl.)	Skrifter udgivne af Videnskabselskabet i Christiania. Mathematisk-naturvidenskabelig Klasse
Christiania, Univers Lab.	Das chemische Laboratorium der Universitat Christiania
Chron. ind.	Chronique de l'industrie
Chur, Jahresber. Naturf Gesell.	Jahresbericht der Naturforschenden Gesellschaft von Graubunden in Chur
Ciment	Ciment, Le
Cincin Soc Natu Hist JI	The Journal of the Cincinnati Society of Natural History
Cistula Entom	Cistula Entomologica
Civil Eng. Inst Trans.	Transactions of the Institution of Civil Engineers
Civil Eng. J.	The Civil Engineer and Architect's Journal, etc.
Civilingenieur	Der Civilingenieur
Clay Worker	Clay Worker, The
Clermont, Mem. Acad. Sci	Memoires de l'Academie des Sciences, Belles Lettres, Arts de Clermont-Ferrand
Cleveland Med J.	Cleveland Medical Journal
Clin Soc Trans.	Transactions of the Clinical Society of London
Coblentz, Jahr. bot. Ver.	Jahresbericht des botanischen Vereines am Mitten und Niederrheine, mit botanischen Abhandlungen
Cohn, Beitr Biol. Pflanz.	Beitrage zur Biologie der Pflanzen
Coimbra, Inst.	O Instituto, journal scientifico et letterario
Coimbra, Soc. Broter. Bol.	Sociedade Broteriana. Boletim Anual
Col P.	Colombian Patent
Collegium	Collegium (Scientific technical supplement to Ledermarkt)
Colliery Guardian	Colliery Guardian and Journal of the Iron and Coal Trades
Colmar Soc. Hist. Natur. Bull.	Bulletin de la Société d'Histoire Naturelle de Colmar
Colombia, Contrib.	Contribuciones de Colombia a las Ciencias i a las Artes
Colombo	See Ceylon
Colorado Sci. Soc. Proc.	Proceedings of the Colorado Scientific Society
Comment. Fauna &c. Ven. Trent.	Commentario della Fauna, Flora e Gea del Veneto e Trentino
Compt. rend.	Comptes rendus hebdomadaires des Seances de l'Academic des Sciences

Compt rend Assoc Franc	Association Francaise pour l'Avancement des Sciences. Compte Rendu de la 1 <sup>e</sup> (-12 <sup>e</sup> ) Session, 1872-83
Compt rend. minerale	Comptes rendus de la Société de l'industrie minerale
Compt rend Soc. biol	Comptes rendus des seances et memoires de la Société de biologie, Paris
Compt rend. trav lab Carlsberg	Comptes rendus du travaux du laboratoire de Carls- berg
Concrete	Concrete
Concrete Age	Concrete Age
Concrete Constr Eng	Concrete and Constructional Engineering
Concrete Eng	Concrete Engineering (no longer published separately. Combined with Cement Age)
Conegliano Scuola Vit Enol Ann	Annali della R Scuola di Viticoltura e di Enologia in Conegliano
Conegliano Scuola Vit Enol N Rassegna	Nuova Rassegna di Viticoltura de Enologia della R. Scuola di Conegliano
Conegliano Scuola Vit Enol Riv	La Rivista Periodico (quindicinale, Organo) della R Scuola di Viticoltura e di Enologia (e del Comizio Agrario) di Conegliano
Cong P	Congo Free State Patent
Congr Anthropol Compt Rend	Congres international d'Anthropologie et d'Archeologie prehistoriques Comptes Rendus
Congr Bot Crittog Atti	Societa Crittogamologica Italiana. Atti del Congresso Nazionale di Botanica Crittogamica in Parma
Congr Bot Int Atti	Atti del Congresso Internazionale di Genova
Congr Int Bot Bull	Bulletin du Congres International de Botanique et d'Horticulture reuni a St Petersburg
Congr Internatl Horti- c Bull	Bulletin du Congres International d'Horticulture a Bruxelles
Congr Internatl. Med. Atti	Atti dell' XI. Congresso Medico Internazionale
Congr Internatl Med C R	Comptes-Rendus du XII Congres International de Medecine
Congr Internatl Sci Med C R	Congres Periodique International des Sciences Medi- cales Compte-Rendu
Congr Internatl Zool (C R)	Congres International de Zoologie
Connecticut, Acad Mem	Memoirs of the Connecticut Academy of Arts and Sciences
Connecticut Acad Trans	Transactions of the Connecticut Academy of Arts and Sciences
Contrib Biol Veg	Contribuzioni alla Biologia Vegetale
Copenhagen	See Kjobenhavn
Copenhagen	See Congr Int Sci Med C R, 1881
Copenhagen, Resumé	Résumé du Bulletin de la Société Royale Danoise des Sciences
Cordoba Acad Bol	Boletin de la Academia Nacional de Ciencias Exactas existente en la Universidad de Cordoba
Cordoba Acad Ci. Act	Actas de la Academia Nacional de Ciencias en Cordoba
Corn Trade J.	Corn Trade Journal
Cornwall, J Roy Inst	Journal of the Royal Institution of Cornwall
Cornwall Poly Soc Rep	Royal Cornwall Polytechnic Society, Annual Report
Cornwall, Poly. Soc Trans.	Reports and Transactions of the Royal Geological Society of Cornwall
Corresp. Blatt. Schweiz Aerzte	Correspondenz-Blatt fur Schweizer Aerzte
Corresp Blatt Zahn. Cosmos	Correspondenzblatt fur Zahnarzte Cosmos Revue Encyclopedique hebdomadaire

Costa, Corrisp Zool.	Corrispondenza Zoologica, destinata a diffondere nel regno delle Due Sicilie tutto cio che si va discuo- pendo entro e fuori Europa (e vice-versa), ris guardante la Zoologia in generale
Cotteswold Club Proc	Proceedings of the Cotteswold Naturalists' Field Club
Cracovie Acad. Sci. Bull	Bulletin International de l'Academie des Sciences de Cracovie
Cracow	See Krakow
Crell. Ann.	Chemische Annalen fur die Freunde der Naturlehre, etc
Crichton, Russ. Sammlung	Russische Sammlung fur Naturwissenschaft und Heilkunst
Cron. med. mex.	Cronica medica mexicana, Mexico
Croydon Micro Club Proc	Proceedings and Transactions of the Croydon Micro- scopical and Natural History Club
Croydon Micro Club Rep	Report and Abstract of Proceedings of the Croydon Microscopical (and Natural History) Club
Cuba P.	Cuban Patent
Cuba, Rep. Fis. Nat.	Repertorio fisico-naturale de la isla de Cuba
Cuir	Cuir, Le
Cumberland Assoc. Trans.	Transactions of the Cumberland and Westmorland Association for the Advancement of Literature and Science
Cuyper, Rev. Univ.	Revue Universelle des Mines, de la Metallurgie, &c.
D'Alton u. Burm. Ztg Zool.	Zeitung fur Zoologie, Zootomie, und Palaeozoologie
Dan. Biol. Stat. Rep.	Report of the Danish Biological Station to the Home Department (Board of Agriculture)
Dan. P.	Danish Patent
Danzig, Neu. Schrift.	Neueste Schriften der Naturforschenden Gesellschaft in Danzig
Danzig, Schrift	Schriften der Naturforschenden Gesellschaft in Danzig
Darmst. Beitr. Geol.	Beitrage zur Geologie des Grossherzogthums Hessen und der angrenzenden Gegenden
Darmst. Ver. Erdk. Notiz.	Notizblatt des Vereins fur Erdkunde zu Darmstadt und des Mittelrheinischen Geologischen Vereins
Davenport Acad. Proc	Proceedings of the Davenport Academy of Natural Sciences
Dax Soc. Borda Bull	(Bulletin de la) Société de Borda, Dax (Landes)
Delft Ecole Poly. Ann.	Annales de l'Ecole Polytechnique de Delft
Delhi, Med. J.	Quarterly Medical and Surgical Journal for the North- West Provinces
Denison Univ. Sci. Lab Bull	Bulletin of (the Scientific Laboratories of) Denison University
Dent. Cosmos	Dental Cosmos, Philadelphia
Dent. Digest	The Dental Digest, Chicago
Dent. Rev.	The Dental Review
Deut. Amer. Apoth. Ztg.	Deutsch-Amerikanische Apotheker Zeitung, New York
Deut. Amer. Gewerbeztg.	Illustrierte Deutsch-Amerikanische Gewerbe und In- dustrie-Zeitung (Newark, N. J.)
Deut. Arch. Klin. Med.	Deutsches Archiv. fur Klinische Medizin
Deut. Bot. Ges. Ber.	Berichte der Deutschen Botanischen Gesellschaft
Deut. Bot. Monats.	Deutsche Botanische Monatsschrift.
Deut. Buchdr. Ztg.	Deutsche Buchdrucker-Zeitung
Deut. Eisenbahn Ztg.	Zeitung des Vereins Deutscher Eisenbahn-Verwalt- ungen
Deut. Elektro. Ges.	See Zts. Elektroch.



Deut Entom Zts	Deutsche Entomologische Zeitschrift (formerly <i>Berliner Entomologische Zeitschrift</i> )
Deut Geol Ges Zts	Zeitschrift der Deutschen Geologischen Gesellschaft
Deut Gerber Ztg	Deutsche Gerber Zeitung
Deut Ind Ztg	Deutsche Industrie Zeitung
Deut Klinik	Deutsche Klinik
Deut Mechan Ztg	Deutsche Mechaniker-Zeitung
Deut med Wochenschr	Deutsche medizinische Wochenschrift
Deut Monats	Deutsche Monatshefte
Deut Naturf Ber	Amtlicher Bericht der Versammlung Deutscher Naturforscher und Aerzte
Deut Naturf Festschr	Festschrift für die 59. Versammlung Deutscher Naturforscher und Aerzte
Deut Naturf Tagebl	Tageblatt der Versammlung Deutscher Naturforscher und Aerzte
Deut Naturf. Versamml Ber	Bericht über die Versammlung der Deutschen Naturforscher und Aerzte
Deut Poly Ztg	Allgemeine Deutsche Polytechnische Zeitung (H. Grothe)
Deut Phys Ges Verh	Verhandlungen der Deutschen Physikalischen Gesellschaft
Deut Tech Ztg	Deutsche Techniker Zeitung
Deut Topfer Ziegl Ztg	Deutsche Topfer und Ziegler Zeitung
Deut Vierteljahrschr Oeff Gesundh	Deutsche Vierteljahrsschrift für Gesundheitspflege
Deut Zool Ges	See Zool Anz
Deut Zool. Ges Verh	Verhandlungen der Deutschen Zoologischen Gesellschaft
Deut Zts Chirurg	Deutsche Zeitschrift für Chirurgie
Deut Zts Thiermed	Deutsche Zeitschrift für Thiermedizin und vergleichende Pathologie
Deut Zuckerind	Deutsche Zuckerindustrie
Devon Assoc Trans	Transactions of the Devonshire Association for the Advancement of Science, Literature and Art
Devon & Cornwall Hatur Hist Soc	See Plymouth Inst Trans
Diamant Ztg	Diamant, Glas Industrie Zeitung
Dietet Hyg Gaz	Dietetic and Hygienic Gazette, The
Dijon, Acad Sci Mem	Memoires de l'Academie des Sciences, Arts et Belles Lettres de Dijon
Dijon, J Agric	Journal d'Agriculture de la Cote d'Or
Dijon, Seances Acad.	Seances publiques de l'Academie des Sciences, Arts et Belles-Lettres de Dijon
Dinant, Soc Natur. Bull	Bulletin de la Société des Naturalistes Dinantais
Dingl Poly.	Dinglers Polytechnisches Journal
Donders, Archiv	Archiv für die Hollandischen Beiträge zur Natur- und Heilkunde
Dorpat, Archiv	Archiv für die Naturkunde Liv, Esth, und Kurlands
Dorpat, Biol. Naturk.	Biologische Naturkunde
Dorpat, Naturf Ges	See Arch Nat (Dorpat)
Dorpat, Naturwiss. Abh	Naturwissenschaftliche Abhandlungen aus Dorpat
Dorpat Pharm Inst Arb	Arbeiten des Pharmakologischen Institutes zu Dorpat
Dorpat Sitzber	Sitzungsberichte der Naturforscher-Gesellschaft bei der Universität (Jurjew) Dorpat
Dorpat Schr	Schriften herausgegeben von der Naturforscher Gesellschaft bei der Universität (Jurjew) Dorpat
Dorset Field Club Proc	Proceedings of the Dorset Natural History and Antiquarian Field Club

Douai Mem Soc. Agric	Memoires de la Société d'Agriculture, de Sciences, et d'Arts, seant a Douai
Doubs Soc. Emul Mem.	Memoires de la Société d'Emulation du Departement du Doubs
Dove Rep. Physik.	Repertorium der Physik Enthaltend eine vollständige Zusammenstellung der neuern Fortschritte dieser Wissenschaft
Dresden Ausz. Protokoll.	Auszuge aus den Protokollen der Gesellschaft für Natur- und Heilkunde in Dresden
Dresden Denkschr Naturwiss Ges. Isis	Denkschriften der Naturwissenschaftlichen Gesellschaft Isis zu Dresden
Dresden Entom. Ver. "Iris" Corresp.-Bl	See Iris
Dresden Isis Festschr	Festschrift der Naturwissenschaftlichen Gesellschaft Isis in Dresden
Dresden Isis Sitzber.	Sitzungsberichte und Abhandlungen der Naturwissenschaftlichen Gesellschaft Isis in Dresden
Dresden, Jahr. Natur Heilk.	Jahresberichte für 1858-60 v d Gesellschaft für Natur- und Heilkunde in Dresden
Dresden, Mitth. Poly. Schule	Mittheilungen der K. Sachs Polytechnischen Schule
Dresden, Schr. Ges Mineral	Auswahl aus den Schriften der unter Werner's Mitwirkung gestifteten Gesellschaft für Mineralogie
Dresden, Sitzber. Natur Heilk.	Sitzungsberichte der Gesellschaft für Natur- und Heilkunde
D. R. P.	German Patent (Deutsches Reichs-Patent)
Drug. Circ.	Druggist's Circular
Drug Topics	Drug Topics, New York
Dublin, Geol Soc J.	Journal of the Geological Society of Dublin
Dublin, Hosp. Gaz	Dublin Hospital Gazette
Dublin J. Med. Chem Sci	Dublin Journal of Medical and Chemical Science
Dublin J Med Sci	The Dublin Journal of Medical Science
Dublin Med. Trans.	Dublin Medical Transactions
Dublin Micro Club	See Irish Natur.
Dublin, Natur. Hist Soc Proc.	Proceedings of the Natural History Society of Dublin
Dublin Natur Field Club	See Irish Natur.
Dublin, Pathol Soc Proc	Proceedings of the Pathological Society of Dublin
Dublin Quart J.	The Dublin Quarterly Journal of Science
Dublin Quart. J Med.	Dublin Quarterly Journal of Medical Science
Dublin, Roy. Soc. J	Journal of the Royal Dublin Society
Dublin Soc. J, Dublin Soc Trans.	Transactions and Journal of the Dublin Society
Dublin Soc. Sci. Proc.	The Scientific Proceedings of the Royal Dublin Society
Dublin Soc. Sci. Trans	The Scientific Transactions of the Royal Dublin Society
Dublin, Zool. Bot. Assoc. Proc.	Proceedings of the Dublin University Zoological and Botanical Association
Dudley, Geol. Soc. Proc.	Transactions of the Dudley and Midland Geological and Scientific Society
Dumfr. Gallow. Soc Trans	The Transactions and Journal of Proceedings of the Dumfriesshire and Galloway Natural History and Antiquarian Society
Dunkerque, Mem. Soc. Encour.	Memoires de la Société Dunkerquoise pour l'Encouragement des Sciences, des Lettres, et des Arts
Durham Univ. Phil. Soc. Proc.	Proceedings of the University of Durham Philosophical Society

Dyer, Calico Ptr	Dyer, Calico Printer, Bleacher, Finisher, and Textile Review
Dzondi, Aeskulap	Aeskulap
Eastbourne Natur Hist Soc Papers (& Trans)	Papers (Transactions) of the Eastbourne Natural History Society
Eastbourne Natur Hist Soc Proc	The Sixth Annual Report of the Eastbourne Natural History Society
Eastbourne Natur Hist Soc Trans	Transactions of the Eastbourne Natural History Society
Echange	L'Echange Organe (Mensuel) des Naturalistes de la Region Lyonnaise
Eckhard, Beitr	Beitrage zur Anatomie und Physiologie
Eclairage Elect	L'Eclairage Electrique Revue (hebdomadaire) de l'Electricite
Elect Med J, Cincin	Electric Medical Journal, Cincinnati
Econ Geol	Economic Geology
Ecu P	Ecuador Patent
Edinb Bot Soc Proc	Proceedings of the Botanical Society of Edinburgh for the years 1855-56
Edinb Bot Soc Trans	Transactions of the Botanical Society of Edinburgh
Edinb Field Club Trans	Transactions of the Edinburgh Naturalists' Field Club
Edinb, Fish Bd Rep	Annual Report of the Fishery Board for Scotland
Edinb J Med Sci	Edinburgh Journal of Medical Science
Edinb J Natur Geogr Sci	The Edinburgh Journal of Natural and Geographical Science
Edinb J Sci	The Edinburgh Journal of Science
Edinb Med Chir Soc Trans	Transactions of the Medico-Chirurgical Society of Edinburgh
Edin Med J	Edinburgh Medical Journal
Edinb Mem Wern Soc	Memoirs of the Wernerian Natural History Society
Edinb Monthly J Med Sci	Edinburgh Monthly Journal of Medical Science
Edinb Natur Soc Trans	Transactions of the Edinburgh Field Naturalists' and Microscopical Society, instituted as the Edinburgh Naturalists' Field Club
Edinb N Phil J	The Edinburgh New Philosophical Journal
Edinb Phil J	The Edinburgh Philosophical Journal
Edinb Plin Soc Trans	Transactions of the Plinian Society
Edinb Proc Phys Soc	Proceedings of the Royal Physical Society of Edinburgh
Edinb, Roy Coll Physns Lab Rep	Reports from the Laboratory of the Royal College of Physicians, Edinburgh
Edinb Roy Soc Proc	Proceedings of the Royal Society of Edinburgh
Edinb Roy Soc Trans	Transactions of the Royal Society of Edinburgh
Edinb Trans Scot Soc Arts	Transactions of the Royal Scottish Society of Arts
Eisen Ztg	Eisen Zeitung
Ekaternburg	See Iekaterinenb
Elberfeld Naturwiss, Ver Jahr	Jahres Bericht des Naturwissenschaftlichen Vereins in Elberfeld
Elec Rev	The Electrical Review
Elec Soc Trans.	The Transactions and Proceedings of the London Electrical Society
Elec Telegr Rev	The Electric Telegraph Review
Elec. World	Electrical World
Electrician	The Electrician
Electricite	Electricite
Electrochem. Met. Ind.	Electrochemical and Metallurgical Industry

Elektrochem Zts	Elektrochemische Zeitschrift
Elektrotech Zts	Electrotechnische Zeitschrift
Elliott Soc J.	Journal of the Elliott Society of Natural History
Elliott Soc Proc	Proceedings of the Elliott Society of Natural History
Elsner, Mitth	See Chem Tech. Mitth
Emden Naturf Ges Jahr.	.. Jahresbericht der Naturforschenden Gesellschaft in Emden
Emden Naturf Ges Schr	Kleine Schriften der Naturforschenden Gesellschaft in Emden
Eng.	Engineering
Eng Contr	Engineering and Contracting
Eng. Digest	Engineering Digest
Eng Mag	Engineering Magazine, The
Eng Mining J (Eng Min J)	Engineering and Mining Journal, The
Eng. News	Engineering News
Eng Record	Engineering Record, Building Record and Sanitary Engineer
Engineer	Engineer, The
Engineers' J	The Engineers' Journal and Railway Gazette of India and the Colonies
Engineers Soc Trans	Society of Engineers. Transactions
Engl Mech	English Mechanic
Engler, Bot Jahr	Botanische Jahrbucher fur Systematik, Pflanzengeschichte und Pflanzengeographie
Engrais, L'	Engrais, L'
Entom Annual	The Entomologist's Annual
Entom Mag	The Entomological Magazine
Entom Medd (Kjobenh)	Entomologiske Meddelelser udgivne af Entomologisk Forening
Entom Month Mag.	The Entomologist's Monthly Magazine
Entom. Nachr	Entomologische Nachrichten
Entom Record	The Entomologist's Record and Journal of Variation
Entom Soc. Trans	The Transactions of the Entomological Society of London
Entom Tidskr.	Entomologisk Tidskrift pa Foranstaltande af Entomologiska Foreningarna i Stockholm
Entomologica Amer	Entomologica Americana
Entomologist	The Entomologist
E P	English (British) Patent
Epicure	Epicure, The
Epidem Soc Trans.	Transactions of the Epidemiological Society of London
Epinal (Vosges) Ann	Annales de la Société d'Emulation du departement des Vosges
Erdel Muz -Egyl Ertek.	Az Erdelyi Muzeum-Egyelet Kiadvanyai Ertekezések. (Publications of the Transylvanian Museum Association. Memoirs)
Erdmann, Sveriges Geol. Undersok.	Sveriges geologiska Undersokning, pa offentlig bekostnad, utford under Ledning af A. Erdmann
Erfurt, Abh Akad. Wiss	Abhandlungen der Kurfurstlich Mainzer Akademie nutzlicher Wissenschaften zu Erfurt
Erfurt, Akad Jahr.	Jahrbucher der koniglichen Akademie gemeinnutziger Wissenschaften zu Erfurt
Erfurt, Denkschr.	Denkschrift der Akademie gemeinnutziger Wissenschaften in Erfurt
Erfurt, Nova Acta	Nova Acta Academiae Electoralis Moguntinae Scientiarum utilium quae Erfurti est.

Ergeb. Physiol. Erlangen, Abh.	Ergebnisse der Physiologie, Wiesbaden Abhandlungen der Physikalisch-medicinischen Societät in Erlangen
Erlangen Anat Inst	See Bietr. Morphol
Erlangen, Mitth. Phys. Med. Soc	Wissenschaftliche Mittheilungen der Physikalisch- medizinischen Societät zu Erlangen
Erlangen Phys. Med. Soc. Sitzber.	Sitzungsberichte der Physikalisch-Medizinischen Societät zu (in) Erlangen
Erythea	Erythea. A Journal of Botany, West American and General
Essex Field Club Proc.	Journal of Proceedings of the Essex Field Club
Essex Field Club Spec. Mem	Essex Field Club Special Memoirs
Essex Field Club Trans.	Transactions of the Essex Field Club
Essex Inst. Bull.	Bulletin of the Essex Institute
Essex Inst. Commun.	Communications read before the Essex Institute
Essex Inst. Proc	Proceedings of the Essex Institute
Essex Natur. Hist. Soc. J.	Journal of the Essex County Natural History Society
Essex Natlist.	The Essex Naturalist
Essig. Ind.	Deutsche Essigindustrie
Etudes Gites Mineraux	See France Gites Min Etudes
Eure, Bull. Acad. Ebroic.	Bulletin de l'Academie Ebroicienne
Eure, J. Agric.	Journal d'Agriculture, de Medicine et des Sciences accessoires
Eure, Recueil Trav	Recueil des Travaux de la Société Libre d'Agriculture, des Sciences, des Arts et des Belles-Lettres du departement de l'Eure
Eure, Soc. Agric. Bull.	Bulletin de la Société d'Agriculture, des Sciences, et des Arts du departement de l'Eure
Eure, Soc. Agric. Recueil	Recueil de la Société d'Agriculture, Sciences, Arts, et Belles-Lettres du departement de l'Eurs
Evkönyv	A' Magyar Tudos Tarsasag' Evkönyvei
Exner. Rep.	Repertorium der Physik
Exper. Sta. Rec.	Experiment Station Record
Eyr	Eyr, et Medicinsk Tidsskrift
Fachgenosse	Fachgenosse, Der
Falaise, Mem. Soc. Acad.	Memoires de la Société Academique des Sciences, &c, de Falaise
Farben Ztg.	Farben Zeitung
Farb. Ztg.	Farber Zeitung (Lehne's)
Fechner Centr.	Centralblatt für Naturwissenschaften und Anthro- pologie
Fechner, Rep.	Repertorium der Experimental-Physik.
Fed. Inst. Min. Engin. Trans.	Transactions of the Federated Institution of Mining Engineers
Fer.	Ferrum, Halle
Ferussac, Bull. Sci. Math.	Bulletin des Sciences Mathematiques, Astronomiques, Physiques, et Chimiques par le Baron de Ferussac
Ferussac, Bull. Sci. Natur.	Bulletin des Sciences Naturelles et de Geologie
Feuille Jeunes Natur.	Feuille des Jeunes Naturalistes
Field Mus. Natur. Hist.	Field Museum of Natural History, Chicago, Publica- tion
Fij. P.	Fiji Islands Patent
Fin. P.	Finland Patent
Finistere Soc. Sci. Bull.	Bulletin de la Société d'Etudes Scientifiques du Finistere
Finlande Soc. Geogr.	See Fennia
Finska Läk. Sällsk. Handl.	Finska Läkare Sällskapets Handlingar
Finska Vet.-Soc.	See Helsingfors, Bidrag. Helsingfors, Öfvers

Firenze Accad. Georgofili	Atti della Reale Accademia Economico-Agraria dei Georgofili di Firenze
Firenze, Ann. Mus Fis	Annali del R Museo di Fisica e Storia Naturale
Firenze, Ann. Mus Imp.	Annali del Museo Imperiale di Fisica e Storia Naturale di Firenze
Firenze Congr Bot Atti	Atti del Congresso Internazionale Botanico tenuto in Firenze nel mese di Maggio 1874
Firenze, Mem Soc Ital.	See Modena
Firenze, Opusc Sci	Collezione d'Opuscoli scientifici
Firenze R Inst Pubbl	Pubblicazioni del R Istituto di Studi Superiori Pratici e di Perfezionamento in Firenze
Firenze Soc Georgofili Atti	Atti della (Real) Società Economica di Firenze ossia de' Georgofili
Firenze Soc Studi Geogr. Boll.	See Riv Geogr Ital
Flora	Flora oder Allgemeine Botanische Zeitung
Flore Jardins	Annales d'Horticulture et de Botanique, ou Flore des Jardins du Royaume des Pays-Bas
Flore Serres	Flore des Serres et des Jardins de l'Europe
Florence	See Firenze
Florke, Repert	Repertorium des neuesten und wissenwürdigsten aus der gesammten Naturkunde
Foldt Kozlon	Foldtani Kozlony, Havi folyoirat kiadja a Magyarhoni Foldtani Tarsulat
Folia Clin.	Folia clinica chimico et microscopica
Folia haematol	Folia haematologica
Folia Therap Lond	Folia Therapeutica, London
Forbes, Med. Rev	The British and Foreign Medical Review, or Quarterly Journal of Practical Medicine and Surgery
Forsch Agr -Phys	Forschungen auf dem Gebiete der Agrikultur-Physik
Forster, Allg. Bauztg	Allgemeine Bauzeitung
Fortschr. Chem.	Fortschritte der Chemie, Physik und Physikalischen chemie
Fortschr Med	Fortschritte der Medicin
Fortschr Phys.	Die Fortschritte der Physik
Fortschr. Rontgenstr.	Fortschritte auf dem Gebiete der Rontgenstrahlen
Fortschr. Theerfarben-Fabrikation	Fortschritte der Theerfarbenfabrikation und verwandter Industriezweige
Foundry	Foundry, The
F. P.	French Patent
France, Congr. Med Chir.	Congres Medico-Chirurgicale de France
France, Congr. Sci	Sessions des Congres Scientifiques de France
France Gites Miner. Etudes	Etudes des Gites Mineraux de la France
France, Inst. Provinces	Annuaire de l'Institut des Provinces et des Congres Scientifiques de France
France, Inst. Provinces	Memoires de l'Institut des Provinces de France
Mem.	Sciences physiques et naturelles
France Soc. Agric. Bull.	Bulletin des Seances de la Société Nationale d'Agriculture de France
France Soc. Agric. Mem.	Memoires publies par la Société Nationale d'Agriculture de France
France Soc. Bot. Bull.	Bulletin de la Société Botanique de France
France Soc. Entom.	See Abeille., Paris, Soc. Ent. Ann., Paris, Soc. Ent. Bull., Rev. Ent.
Franc Soc. Miner. Bull.	Bulletin de la Société Mineralogique de France. Bulletin de la Société Francaise de Mineralogie. (Ancienne Société Mineralogique de France)
France Soc. Zool.	See Paris, Caus. Sci.
France Soc. Zool. Bull.	Bulletin de la Société Zoologique de France

France Soc. Zool. Mem.	Memoires de la Société Zoologique de France
Frankfurt	See Senckenberg
Frankfurt, Jahr Phys Ver.	Jahrbuch zur Verbreitung naturwissenschaftlicher Kenntnisse, veranstaltet vom Physikalischen Verein zu Frankfurt a/Main
Frankf Ver Pflege Phot.	See Wien, Photogr Correspond
Frankfurt, Zool Garten	Der Zoologische Garten Frankfurt a/M.
Frankfurter Zts Pathol	Frankfurter Zeitschrift für Pathologie
Franzos Ann	Französische Annalen für die allgemeine Naturgeschichte, Physik, &c.
Freiberg, Jahr Berg Hutt	Jahrbuch für den Berg- und Huttenmann. Herausg. von der Königl Berg-Akademie zu Freiberg
Freiburg, Beitr	Beiträge zur Rheinischen Naturgeschichte
Freiburg, Ber	Berichte über die Verhandlungen der Naturforschenden Gesellschaft zu Freiburg i. B.
Freie K.	Freie Künste
Frelon	Le Frelon Journal d'Entomologie descriptive
Fries, Bot Notiser	Botaniska Notiser
Froriep, Notizen	Notizen aus dem Gebiete der Natur- und Heilkunde
Fuhling's Ztg.	Fuhlings landwirtschaftliche Zeitung
Gac ind	La Gaceta industrial
Gand, Ann Soc Agric	Annales de la Société Royale d'Agriculture et de Botanique
Gand, Ann Soc Med	Annales de la Société de Médecine de Gand
Gand, Bull. Soc Med.	Bulletin de la Société de Médecine de Gand
Gard, Aperçu Trav.	Notice ou Aperçu analytique des Travaux de l'Académie Royale du Gard
Gard, Mem Acad	Memoires de l'Académie du Gard
Gard, Notice Trav. Acad	Notice des Travaux de l'Académie du Gard
Garden & Forest	Garden and Forest A Journal of Horticulture, Landscape Art and Forestry
Gardeners Chron	The Gardeners Chronicle
Garnett, Ann Phil.	Annals of Philosophy, Natural History, Chemistry &c.
Garten-Flora	Garten-Flora
Garten-Ztg.	Neue allgemeine Deutsche Garten- und Blumenzeitung
Gartenwelt	Gartenwelt, The
Gas World	Gas World, The
Gaz	Le Gaz
Gazz. del Clin	Gazzetta della Cliniche
Gazz. med. ital lomb.	Gazzetta medica italiana lombardia, Milano
Gazz. Chim. Ital	Gazzetta Chimica Italiana
Geelong Field Natur. Club	See Wombat
Gehlen J.	Journal für die Chemie und Physik
Gendrin, Trans Med.	Transactions Médicales
Geneeskundig Mag.	Geneeskundig Magazijn
Geneve, Archiv	See Archives Sci. Phys. Nat.
Geneve, Bull. Soc. Ornith Suisse.	Bulletin de la Société Ornithologique Suisse
Geneve Conserv. Bot. Annuaire	Annuaire du Conservatoire du Jardin Botanique de Geneve
Geneve, Inst Natl. Bull.	Bulletin de l'Institut National Genevois
Geneve, Inst. Natl. Mem.	Memoires de l'Institut National Genevois
Geneve, Mus. Hist. Natur Ann.	See Rev. Suisse Zool.
Geneve, Recueil Trav. Soc. Med.	Recueil des Travaux de la Société Médicale de Geneve
Geneve, Soc. Geogr. Mem.	Memoires de la Société de Géographie de Geneve

Geneve, Soc Phys Mem	Memoires de la Société de Physique et d'Histoire Naturelle de Geneve
Genie civ.	Genie Civil
Genova	See Congr Bot Int Atti 1892
Genova, Ann Mus Phys	Annali del Museo Civico di Storia Naturale
Genova, Giorn	Giornale degli Studiosi di Lettere, Scienze, arti e Mestieri
Genova, Mem. Accad	Memoire dell'Accademia Imperiale delle Scienze di Genova
Genova, Mem Ist. Ligure.	Memorie dell' Istituto Ligure
Genova, Mem. Soc. Med. Emul.	Memorie della Societa Medica di Emulazione di Genova
Genova Mus Civ. Ann	Annali del Museo Civico di Storia Naturale di Genova
Genova Mus Zool Anat Comp Boll	Bollettino dei Musei di Zoologia e Anatomia Comparata della R. Università di Genova
Genova, Soc Ligust Atti	Atti della Societa Ligustica di Scienze Naturali e Geografiche
Genova Univ Atti	Atti della R. Università di Genova
Geogr. Soc J.	Journal of the Royal Geographical Society of London
Geogr. Soc Proc	Proceedings of the Royal Geographical Society and Monthly Record of Geography
Geogr Soc Suppl Pap	Royal Geographical Society. Supplementary Papers
Geol Mag	Geological Magazine
Geol Survey, Can	Geological Survey, Canada
Gera, Naturwiss Jahr	Jahresbericht der Gesellschaft von Freunden der Naturwissenschaften in Gera, nebst Nachrichten über den Naturwissenschaftlichen Verein in Schleiz
Gerber	Der Gerber
Germar, Mag Entom	Magazin der Entomologie
Germar, Zts Entom	Zeitschrift für die Entomologie
Gergonne, Ann Math	Annales de Mathematique
Gesundh Ing.	Gesundheits-Ingenieur
Gew. Ztg	Wick's Gewerbezeitung
Gewerbebl Schw.	Schweizerisches Gewerbeblatt
Gewerbebl Wurt	Gewerbeblatt aus Württemberg
Gewerbebl	Gewerbehalle
Gewerks Ztg	Oesterreichische Gewerkszeitung
Giessen, Oberhess Ges. Ber.	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde
Gievel, Zts.	See Zts Gesamt. Naturwiss.
Gilbert, Ann Phys	See Ann Phys.
Gill, Tech Micro Repos	Technical and Microscopical Repository
Giorn. Arcad	Giornale Arcadico di Scienze
Giorn. farm chim.	Giornale de farmacia, di chimica
Giorn Gen civ	Giornale del Genio civile
Giron. Ist. Lomb	See Bibl Ital
Giorn Mineral Crist Petr.	Giornale di Mineralogia, Cristallografia e Petrografia
Gironde Comm. Meteorol.	See Bordeaux Soc. Sci. Mem.
Gironde, J. Med.	Journal Medical de la Gironde
Gistl, Faunus	Faunus
Glasgow. Inst. Engin. Trans.	Transactions of the Institution of Engineers and Ship-builders in Scotland
Glasgow Med. Chir. Soc. Trans.	Transactions of the Medico-Chirurgical Society of Glasgow
Glasgow Med. J.	Glasgow Medical Journal
Glasgow Natur. Hist. Soc. Proc. & Trans.	Proceedings and Transactions of the Natural History Society of Glasgow
Glasgow Path. Clin. Soc. Trans.	Transactions of the Glasgow Pathological and Clinical Society



Glasgow Phil Soc Proc	Proceedings of the Philosophical Society of Glasgow
Glashutte	Glashutte, Die
Glas-Ind.	Glas-Industrie, Die
Gleanings Sci	Gleanings in Science
Globe	See Geneve Soc Geogr Mem.
Glückauf	Gluckauf; Berg- und Huttenmannische-Zeitschrift
Good Roads	Good Roads
Goodsir, Ann. Anat. Physiol	Annals of Anatomy and Physiology
Gordon Coll. Phot. Assoc.	See Wombat.
Görlitz, Abh.	Abhandlungen der Naturforschenden Gesellschaft zu Görlitz
Götheborg, Handl	Gotheborgs Kongl Vetenskaps och Vitterhets Samhälles Handlingar
Götheborg, Nya Handl	Nya Handlingar af Kongl. Vettenskaps och Vitterhets Samhället i Gotheborg
Gottingen, Abh.	Abhandlungen der Königlichen Gesellschaft der Wissenschaften zu Gottingen
Göttingen, Comment.	Commentationes recentiores Societatis, etc
Göttingen, Nachr.	Nachrichten von der Georg-Augusts Universität und der Königl Gesellschaft der Wissenschaften zu Göttingen
Göttinger Studien	Gottinger Studien
Göttingen, Studien Ver.	Studien des Gottingischen Vereins Bergmannischer Freunde
Gräfe, J. Chir. Augenheilk.	Journal der Chirurgie und Augen-Heilkunde
Graph. Mitth.	Schweizer graphische Mitteilungen
Graubünden Naturf. Ges. Jahr.	Jahresbericht der Naturforschenden Gesellschaft Graubündens
Gravenhage, Athenaeum	Athenaeum
Gravenhage, Inst. Ingen. Tijdschr.	Tijdschrift van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen. Uittrek.	Uittreksels uit Vreemde Tijdschriften voor de Leden van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen. Verh.	Verhandelingen van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen. Verslag.	K. Instituut van Ingenieurs Algemeen Verslag van de Werkzaamheden en Notulen der Vergaderingen
Gravenhage, Tijdschr.	Tijdschrift voor Entomologie, door de Nederlandsche Entomologische Vereeniging
Graves, Natur. J.	The Naturalists' Journal and Miscellany
Graz Bot. Inst. Mitth.	Mittheilungen aus dem Botanischen Institute zu Graz
Graz, Unters. Physiol. Histol.	Untersuchungen aus dem Institute für Physiologie und Histologie
Great. Brit. Phil. Soc.	See Victoria Inst J.
Greifswald Naturwiss. Ver. Mitth.	See Neu-Vorpommern Mitth.
Grenoble, Acad. Delph. Bull.	Bulletin de l'Academie Delphinale, ou Société des Sciences et Arts de Grenoble
Grevillea	Grevillea, a Quarterly Record of Cryptogamic Botany and its Literature
Groningen, Ann. Acad.	Annales Academiae Groninganae
Gruithuisen, Neue Analect.	Neue Analecten für Erd- und Himmelskunde
Grunert Archiv.	Archiv für Mathematik und Physik
Grunert, Meteor. Optik	Beiträge zur meteorologischen Optik, etc.
Guat. P.	Guatemala Patent

Guia Minero	Guia del Minero. Periodico científico, industrial y mercantil
Guillemin, Archiv. Bot	Archives de Botanique, ou Recueil Mensuel de Mémoires originaux, etc.
Gummi-Ztg.	Gummi-Zeitung
Gunsburg, Zts. Klin. Med.	Zeitschrift für klinische Medizin, mit dem Verein für physiologische Heilkunde in Breslau
Gurlt, Mag. Ges. Thierheilk.	Magazin für die gesammte Thier-Heilkunde
Guy's Hosp. Rep.	Guy's Hospital Reports
Haarlem Kolon. Mus. Bull.	Bulletin van het Koloniaal Museum te Haarlem
Haarlem, Mus. Teyler Archiv.	Archives du Musée Teyler
Haarlem, Natuurk. Verh. Maatsch. Wet.	Natuurkundige Verhandelingen van de (Bataafsch) Hollandsche Maatschappij der Wetenschappente Haarlem
Haaxman, Tijdschr.	Tijdschrift voor Wetenschappelijke Pharmacie, etc.
Habana Acad. Anales.	Anales de la (Real) Academie de Ciencias Medicas Físicas y Naturales de la Habana
Haeser, Archiv. Med.	Archiv für die gesammte Medicin
Hage	See Gravenhage
Hahnemann Month.	Hahnemannian Monthly, Philadelphia
Haidinger, Abh.	Naturwissenschaftliche Abhandlungen
Haidinger, Ber.	Berichte über die Mittheilungen von Freunden der Naturwissenschaften in Wien
Hainaut Soc. Mem.	Mémoires et Publications de la Société des Sciences, des Arts et des Lettres du Hainaut
Hall, Bijdragen	Bijdragen tot de Natuurkundige Wetenschappen
Halle, Abr. Naturwiss. Ver.	Abhandlungen des Naturwissenschaftlichen Vereins für Sachsen und Thüringen in Halle
Halle aux cuirs, La	Halle aux cuirs, La
Halle, Jahr. Naturwiss. Ver.	Jahresbericht des Naturwissenschaftlichen Vereins in Halle
Halle Kryptog. Lab.	See Beitr. Physiol. Morphol.
Halle, Naturf. Ges. Abh.	Abhandlungen der Naturforschenden Gesellschaft zu Halle
Halle, Naturf. Ges. Ber.	Bericht der Naturforschenden Gesellschaft zu Halle
Halle, Naturf. Ges. Neu. Schr.	Neue Schriften der Naturforschenden Gesellschaft zu Halle
Halle, Zts. Ges. Naturwiss.	Zeitschrift für die gesammten Naturwissenschaften
Hamburg, Abh. Geb. Naturwiss.	Abhandlungen aus dem Gebiete der Naturwissenschaften
Hamburg Bot. Ges.	See Bot. Centrbl.
Hamburg, Mitth.	Mittheilungen aus den Verhandlungen der Naturwissenschaftlichen Gesellschaft in Hamburg
Hamb. Mus. Ber.	Naturhistorisches Museum zu Hamburg. Berichte
Hamb. Mus. Jahr.	Jahresbericht über das Naturhistorische Museum zu Hamburg
Hamb. Mus. Mitth.	Mittheilung aus dem Naturhistorischen Museum in Hamburg
Hamb. Naturwiss. Ver. Abh.	Abhandlungen aus dem Gebiete der Naturwissenschaften herausgegeben vom Naturwissenschaftlichen Verein in Hamburg
Hamb. Ver. Naturwiss. Unterh. Verh.	Verhandlungen des Vereins für Naturwissenschaftliche Unterhaltung zu Hamburg
Hamb. Wiss. Anst. Jahr.	Jahrbuch der Hamburgischen Wissenschaftlichen Anstalten

Hampshire Field Club Pap. & Proc.	Papers and Proceedings of the Hampshire Field Club
Hannover Architekt.-Ver. Zts.	Zeitschrift des Architekten- und Ingenieur-Vereins zu Hannover. Zeitschrift für Architektur und Ingenieurwesen
Hannover Jahr.	... Jahresbericht der Naturhistorischen Gesellschaft zu Hannover
Hannoverische Ann.	Hannoverische Annalen für die gesammte Heilkunde
Harlem Soc. Holland Sci.	See Arch. Neerland
Hartford, Trans.	Transactions of the Natural History Society of Hartford
Harvard Mus. Zool. Mem.	Memoirs of the Museum of Comparative Zoology at Harvard College
Harvard Mus. Zool. Bull.	Bulletin of the Museum of Comparative Zoology at Harvard College, in Cambridge
Harz, Naturwiss. Ver. Ber.	Berichte des Naturwissenschaftlichen Vereins des Harzes zu Blankenburg
Havre, Cercle Bot.	Cercle pratique d'Horticulture et de Botanique de l'arrondissement du Havre. Bulletins
Haw. P.	Hawaiian Patent
Haye	See Congr. Int. Hyg. C. R., 1884
Heart	Heart
Hedwigia	Hedwigia. Ein Notizblatt für Kryptogamische Studien nebst Repertorium für Kryptogamische Literatur. Hedwigia. Organ für (specielle) Kryptogamenkunde (und Phytopathologie) nebst Repertorium für (Kryptogamische) Literatur
Heidelb. Jahr. Lit.	Jahrbücher der Literatur. Verhandlungen des Naturhistorisch-Medicinischen Vereins zu Heidelberg
Heidelb. Naturhist. Med. Festschr.	Festschrift zur Feier des funfhundertjährigen Bestehens der Ruperto-Carola dargebracht von dem Naturhistorisch-Medicinischen Verein zu Heidelberg
Heidelb. Naturhist. Med. Verh.	Verhandlungen des Naturhistorisch-Medicinischen Vereins zu Heidelberg
Heidelb., Verh.	Verhandlungen der in Heidelberg versammelten Augenärzte
Heis, Wochenschr.	Wochenschrift für Astronomie, Meteorologie, und Geographie
Heller, Archiv.	Archiv für physiologische und pathologische Chemie und Mikroskopie
Helsingfors, Acta Soc. Sci. Fenn.	Acta Societatis Scientiarum Fennicae
Helsingfors, Bidrag Finlands Natur o. Folk	Bidrag till kannedom om Finlands Natur och Folk, utgifna af Finska Vetenskaps-Societeten
Helsingfors, Bidrag Finlands Naturkann.	Bidrag till Finlands Naturkannedom, Etnografi och Statistik, utgifna af Finska Vetenskaps-Societeten
Helsingfors, Faun. Flor. Fenn. Acta.	Acta Societatis pro Fauna et Flora Fennica
Helsingfors, Fauna Flora Fenn. Medd.	Meddelanden af Societas pro Fauna et Flora Fennica
Helsingfors, Faun. Flor. Fenn. Notiser	Notiser ur Sällskapets pro Fauna et Flora Feennica Forhandlingar
Helsingfors, Öfers, Finaka Vet. Soc.	Öfersigt af Finska Vetenskaps-Societätens Forhandlingar
Helv. Chim. Acta	Helvetica Chimica Acta
Henle und Pfeufer, Zts.	See Zeitschrift für rationelle Medicin
Hermannstader Verh.	Verhandlungen und Mittheilungen des Siebenburgischen Vereins für Naturwissenschaften in Hermannstadt

Hermbstatt, Archiv.	Archiv der Agriculturchemie fur denkende Landwirthe
Hermstadt, Bull.	Bulletin des Neuesten und Wissenwurdigsten aus der Naturwissenschaft, etc
Hermbstadt, Museum	Museum des Neuesten und Wissenwurdigsten aus dem Gebiete der Naturwissenschaft, der Kunte, der Fabriken, der Manufakturen, der technischen Gewerbe, der Landwirthschaft, der Produktenwaaren und Handelskunde, und der burgerlichen Haushaltung, &c.
Hertha	Hertha
Herts. Natur. Hist. Soc. Trans.	Transactions of the Hertfordshire Natural History Society and Field Club
Hessen, Naturhist. Verg.	Verhandlungen des Naturhistorischen Vereins fur das Gross herzogthum Hessen und Umgebung
Heusinger, Zts.	Zeitschrift fur die organische Physik
Hide and Leather	Hide and Leather
High Wycombe Natur. Hist. Mag	The Quarterly Magazine of the High Wycombe Natural History Society
Highland Soc Trans.	Transactions of the Highland and Agricultural Society of Scotland with an abstract of the Proceedings
Hildesheim Roemer-Mus Mitth.	Mittheilungen aus dem Roemer-Museum Hildesheim
Himly, Bibl. Ophthalm.	Bibliothek fur Ophthalmologie
Hippone	See Bone
Hisinger, Afh.	Afhandlingar i Fysik, Kemi, och Mineralogie
Hobart Town	See Tasmania
Hoeven en Vriese, Tijdschr.	Tijdschrift voor Natuurlijke Geschiedenis en Physiologie
Hoff, Mag.	Magazin fur die gesammte Mineralogie, Geognosie, etc.
Hoffman, Phytogr. Blatt	Phytographische Blatter
Holl. P.	Holland Patent
Holland, Beitr.	Hollandsche Beitrage zu den anatomischen und physiologischen Wissenschaften
Holland, Mag.	Hollandsches Magazin der Naturkunde
Holmesdale Natur. Hist. Club Proc.	Proceedings and Annual Reports of the Holmesdale Natural History Club, Reigate, for the years 1865-67
Homme	L'Homme. Journal illustre des Sciences Anthropologiques
Hooker, Bot. Miscell.	The Botanical Miscellany
Hooker, Comp. Bot. Mag	Companion to the Botanical Magazine
Hooker, Lond. J. Bot.	London Journal of Botany
Hoppe, Bot. Taschenb	Neues Botanisches Taschenbuch fur die Anfanger dieser Wissenschaft und der Apothekerkunst
Horae Soc. Entom. Rossicae	Horae Societatis Entomologicae Rossicae varis sermonibus Rossicae usitatis
Horkel, Archiv.	Archiv. fur die thierische Chemie
Horn, Archiv. Med.	Archiv. fur praktische Medizin und Klinik
Horn's Phot. J.	Horn's photographisches Journal
Hornschuch, Archiv.	Archiv Skandinavischer Beitrage zur Naturgeschichte
Horolog. J.	The Horological Journal
Hortic. Soc. J.	Journal of the Royal Horticultural Society of London
Hortic. Soc. Trans.	Transactions of the Horticultural Society of London
Hufeland, J. Arzn.	Journal der practischen Arzeneikunde
Humboldt.	Humboldt. Monatsschrift fur die Gesamten Naturwissenschaften
Humming Bird	The Humming Bird. . . . scientific, artistic and industrial Review

Hongkong P.	Hongkong Patent
Hung. P.	Hungarian Patent
Hutm. Ztg.	Deutsche Hutmacher-Zeitung
Hyg. Congr.	See Congr. Int. Hyg. Act; Congr. Int. Hyg. C. R.; Int. Congr. Hyg. Arb.; Int. Congr. Hyg. Trans
Hyg. Rundschau.	Hygienische Rundschau, Berlin
Hyg. viande	Hygiène de la viande et du lait, L'
Iekaterinenb., Soc. Oural.	Bulletin de la Société Ouraliennne d'Amateurs des Bull. Sciences Naturelles
Il Berico	Il Berico
Il Cimento	Il Cimento
Il. Giamb-Vico	Il Giambattista-Vico
Il Progresso	Il Progresso delle Scienze, Lettere, ed Arti
Il Subalpino	Il Subalpino, Giornale di Scienze
Il Tempo	Il Tempo, Giornale Italiano di Medicina
III. Insects Rep	. . . Report of the State Entomologist on the Noxious and Beneficial Insects of the State of Illinois
III. Lab. Natur. Hist. Bull.	Bulletin of the Illinois State Laboratory of Natural History
III. Mus. Natur. Hist. Bull.	Bulletin of the Illinois State Museum of Natural History
Illiger, Magazin	Magazin für Insektenkunde
Illumin. Engin. (London)	Illuminating Engineer (London), The
Illust. Hortic.	Illustration horticole, journal special des Serres et des Jardins
Illust. landw. Ztg.	Illustrirte landwirtschaftliche Zeitung
Illust. Off. J.	Illustrated Official Journal, The (Patents)
Illust. Wochenschr. Entom.	Illustrierte Wochenschrift für Entomologie Inter- nationales Organ für alle Interessen der Insekten- kunde. Offizielles Organ der Berliner Entomolo- gischen Gesellschaft
Impr.	L'imprimerie
Ind. Chim.	Industria chimica
Ind. lait.	L'Industrie laitière
Ind. Text.	L'industrie textile
Ind. Ztg.	Deutsche Industrie Zeitung
Index Med.	Index Medicus, Washington
India Agric. Soc. J.	Journal of the Agricultural and Horticultural Society of India
India, Agric. Soc. Proc.	Proceedings of the Agricultural and Horticultural Society of India
India Agric. Soc. Trans.	Transactions of the Agricultural and Horticultural Society of India
India Bot. Surv. Records	Records of the Botanical Survey of India
India Dept. Agric.	India Department of Agriculture, Publications
India, Govt. Records (For. Dept.)	Selections from the Records of the Government of India. (Foreign Department)
India, Govt. Records (Home Dept.)	Selections from the Records of the Government of India
India P.	Indian Patent
India Rev.	India Review and Journal of Foreign Science and the Arts
India Rub. J.	India Rubber Journal
India Rub. World	India Rubber World
Indian Ann.	Indian Annals of Medical Science
Indian J. Med. Phys. Sci.	Indian Journal of Medical Science
Indian Med. Gaz.	The Indian Medical Gazette, a monthly record of Medicine, &c.

Indian Meteorol. Mem.	Indian Meteorological Memoirs: being occasional Discussions and Compilations of meteorological data relating to India and the neighboring countries
Indian Mus. Notes	Indian Museum Notes
Industrietzg. Ungarn	Industriezeitung für Ungarn
Ingenieur	Der Ingenieur
Inghirami, Opuscoli	Nuova Collezione di Opuscoli e Notizie di Scienze
Innsbruck, Jahr.	Jahresbericht der k. k. Ober-Realschule zu Innsbruck
Innsbruck Naturwiss. Med. Ber.	Berichte des Naturwissenschaftlich-medizinischen Vereines in Innsbruck
Innsbruck, Neue Zts	Neue Zeitschrift des Ferdinandeums für Tirol
Innsbruck, Zts. Ferdinandeums	Zeitschrift des Ferdinandeums für Tirol und Voralberg
Inst.	L'Institut
Inst. Act. J.	Journal of the Institute of Actuaries (and Assurance Magazine)
Inst. Brewing Trans	Transactions of the Institute of Brewing
Inst. Civ. Eng. Proc.	Minutes of the Proceedings of the Institution of Civil Engineers
Inst. Egypt. Bull	Bulletin de l'Institut Egyptien
Inst. Egypt. Mem.	Memoires (ou Travaux originaux) presentes (et lus) a l'Institut Egyptien
Inst. Elect. Engin. J.	Journal of the Institution of Electrical Engineers
Inst. Mechan. Engin Proc.	Institution of Mechanical Engineers. Proceedings
Inst. Min Eng Trans	Transactions of the Institution of Mining Engineers
Inst. Min Met Trans	Transactions of the Institution of Mining and Metallurgy
Inst. Solvay Trav.	Institut Solvay. Travaux de Laboratoire
Intell Observer	The Intellectual Observer
Intl. Beitr. Path. Therap.	Internationale Beiträge zur Pathologie und Therapie, die Ernährungsstörungen, Stoffwechsel und Verdauungskrankheiten
Intl Congr Appl Chem.	International Congress of Applied Chemistry
Intl. Congr Hyg. Trans.	Transactions of the International Congress of Hygiene and Demography
Intl. Congr Zool Proc.	Proceedings International Congress of Zoology
Intl. Entom Ver.	See Zurich, Soc. Ent.
Intl. Med. Congr Trans	Transactions of the International Medical Congress
Intl Med. Congr Verh.	Verhandlungen des Internationalen Medicinischen Congresses
Intl. J. Anat.	Monthly International Journal of Anatomy and Histology (Physiology)
Intl. Mschr. Anat.	See Intl. J. Anat.
Intl Sugar J.	International Sugar Journal, The
Intl. Zentr. Baukeram. Glasind.	Internationales Zentralblatt für Baukeramik und Glasindustrie
Intl. Zts. Metallog.	Internationale Zeitschrift für Metallographie
Invent. Rec.	Inventor's Record, The
Iowa Acad. Sci. Proc.	Proceedings of the Iowa Academy of Sciences
Iowa Univ. Lab. Natur. Hist. Bull.	Bulletin from the Laboratories of Natural History of the State University of Iowa
Ireland, Coll. Physicians Trans.	Transactions of the Association of Fellows and Licentiates of the King's and Queen's College of Physicians in Ireland
Ireland, Inst. Civ. Eng. Trans.	The Transactions of the Institute of Civil Engineers of Ireland

- Ireland Roy. Soc. Ant. See Dublin, Roy. Soc. Ant. Ir. JI  
 Proc & Pap.  
 Ireland Zool. Soc. See Irish Natlist  
 Iris Correspondenz-Blatt des Entomologischen Vereins  
 Iris zu Dresden Iris, Dresden Deutsche Entomologische Zeitschrift herausgegeben von der Gesellschaft Iris zu Dresden in Verbindung mit der Deutschen Entomologischen Gesellschaft zu Berlin .  
 Fortsetzung des "Correspondenz-Blattes des Entomologischen Vereins Iris."
- Irish Acad. Cunningham Royal Irish Academy. Cunningham Memoirs  
 Mem.  
 Irish Acad. Proc. Proceedings of the Royal Irish Academy  
 Irish Acad. Trans The Transactions of the Royal Irish Academy  
 Irish Natur. The Irish Naturalist: a monthly Journal of general  
 Irish Natural History
- Iron  
 Iron Age  
 Iron Coal Trades Rev. Iron Coal Trades Review  
 Iron Steel Inst. J. The Journal of the Iron & Steel Institute  
 Iron Steel Inst Trans Transactions of the Iron and Steel Institute  
 Isenflamm, Beitr. Zerg-  
 lied Beitrage fur die Zergliederungskunst
- Isere Soc Bull. Bulletin de la Société de Statistique, des Sciences  
 naturelles et des Arts industriels du Departement de  
 l'Isere
- Isle of Man Natur Hist & See Yn Lloar Manninagh  
 Antiq. Soc.
- Italia P.  
 Italia, Soc Bot Bull. Bullettino della Societa Botanica Italiana  
 Italia Soc Crittog Atti Atti della Societa Crittogamologica Italiana  
 Italia Soc. Crittog Com-  
 ment Commentario della Societa Crittogamologica Italiana
- Italia Soc Crittog Mem Memorie della Societa Crittogamologica Italiana  
 Italia, Soc Entom Bull Bullettino della Societa Entomologica Italiana  
 Italia, Soc Zool Boll Bollettino della Societa Zoologica Italiana  
 Ithaca, Cornell Univ Bull  
 Amer Paleont. Bulletins of American Paleontology
- J.  
 J. A. C. S. Journal  
 J. Adv. Therap. Journal of the American Chemical Society  
 J Agric Journal of Advanced Therapeutics, New York  
 J. agric. Hort The (Quarterly) Journal of Agriculture  
 J. Agric. Prat Journal de l'Agriculture, le Horticulture, etc  
 J. Agric. Sci. Journal d'Agriculture pratique, etc.  
 J. agric Soc Journal of Agricultural Science  
 J. Agric Tropicale Journal of the Agricultural Society  
 J. allied Soc. Journal d'Agriculture tropicale  
 J. Amer. Lea. Chem. As-  
 soc. Journal of the Allied Societies (Dental)  
 J. Amer. Med. Assoc. Journal of the American Leather Chemists' Associa-  
 tion  
 J. Amer. Pharm Assoc. Journal of the American Medical Association  
 J. Amer. Soc. Mechan  
 Eng. Journal of the American Pharmaceutical Association  
 J. Anal. Chem. Journal of the American Society of Mechanical Engi-  
 neers  
 J. Anat. The Journal of Analytical (and Applied) Chemistry  
 Journal de l'anatomie de la Physiologie normales et  
 pathologiques de l'homme et des animaux
- J. Anat. Physiol. The Journal of Anatomy and Physiology  
 J. Appl. Chem. Journal of Applied Chemistry

J. Appl. Micr	Journal of Applied Microscopy
J. Assoc. Eng. Soc.	Journal of the Association of Engineering Societies
J. Biol. Chem.	Journal of Biological Chemistry
J. Bot.	Journal de Botanique
J. Buchdr.	Journal für Buchdruckerkunst
J. C. S.	Journal of the Chemical Society, London
J. Camera Club	Journal of the Camera Club
J. Can. Min. Inst.	Journal of the Canadian Mining Institutes
J. Chem. Met. Soc. South Af.	Journal of the Chemical, Metallurgical and Mining Society of South Africa
J. chim. med.	Journal de chimie medicale, de pharmacie et de toxicologie
J. chim. phys.	Journal de chimie, physique, electrochemie, thermo-chimie, radiochimie, mecanique, chimie, stoichiometrie
J. Chir.	Journal de Chirurgie
J. Chir. Augenheilk	Journal der Chirurgie und Augenheilkunde
J. Coll. Agric. Imp Univ. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo
J. Comp. Path Therap	The Journal of Comparative Pathology and Therapeutics
J. Conch.	The Journal of Conchology
J. ecole poly.	Journal de l'Ecole polytechnique
J. Entom.	Journal of Entomology, descriptive and geographical
J. Exp. Med.	Journal of Experimental Medicine
J. Exp. Zool.	Journal of Experimental Zoology, The
J. fabr. sucre	Journal des fabricants de sucre
J. Frank Inst	Journal of the Franklin Institute
J. Gasbeleucht	Journal für Gasbeleuchtung
J. Gaslighting	Journal of Gas Lighting
J. Gen. Physiol.	Journal of General Physiology
J. Genie Civ.	Journal du Genie Civil des Sciences et des Arts
J. Geol.	Journal of Geology
J. Goldschm.	Journal der Goldschmiedekunst und verwandter Gewerbe
J. Heb. Med	Journal Hebdomadaire de Medecine
J. Heb. Sci. Med.	Journal Hebdomadaire des Progres des Sciences et Institutions Medicales
J. Home Econ.	Journal of Home Economics, The
J. Hygiene	Journal of Hygiene
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry
J. Indian Archipel.	Journal of the Indian Archipelago and Eastern Asia
J. Infect. Dis	Journal of Infectious Diseases
J. Inst. Brewing	Journal of the Institute of Brewing
J. Inst. Metals	Journal of the Institute of Metals
J. Intl. Anat.	See Int. J. Anat.
J. Invent.	Journal des Inventeurs
J. Landw.	Journal für Landwirtschaft
J. Med. Chir. Pharm.	Journal de Medecine, Chirurgie, Pharmacie
J. Med. Paris	Journal de medicine de Paris
J. Med. Research	Journal of Medical Research
J. Microgr.	Journal de micrographie
J. Micro. Sci.	Quarterly Journal of Microscopical Science
J. Mines	Journal des Mines, ou Recueil de Memoires sur l'exploitation des Mines, et sur les Sciences et les Arts qui s'y rapportent
J. mines met.	Journal des mines et de metallurgie
J. Morphol.	Journal of Morphology



J. Mus. Godeffroy	Journal des Museum Godeffroy. Geographische, Ethnographische und Naturwissenschaftliche Mittheilungen
J. Mycol.	The Journal of Mycology
J. N. Engl. Water Works Assoc	Journal New England Water Works Association
J. Ophthalmol.	Journal d'Ophthalmologie
J. Ornith.	Journal fur Ornithologie
J. Papier	Journal de Fabricants de Papier, fonde et publie par L. Piette
J. Path Bact	The Journal of Pathology and Bacteriology
J. Petrole	Journal du petrole
J. Pharm.	Journal de Pharmacie
J. Pharm Anvers	Journal de Pharmacie d'Anvers
J. Pharm Chim	Journal de Pharmacie et de Chimie
J. Pharm. Elsass-Lothringen	Journal de pharmacie von Elsass-Lothringen
J. Pharm Soc Japan	Yakagakuzasshi (Journal of the pharmaceutical society of Japan)
J. Pharmacol.	Journal of Pharmacology and Experimental Therapeutics
J. Phot. Suppl	Journal of Photographic Supplies
J. Phot. Soc.	Journal of the Photographic Society
J. Phys.	Journal de Physique theorique et appliquee
J. Phys Chem	The Journal of Physical Chemistry
J. Phys. Chim.	Journal de Physique, de Chimie, et de l'Histoire Naturelle
J. Physiol.	The Journal of Physiology
J. physiol. path gen.	Journal de physiologie et de pathologie general, Paris
J. prakt. Chem	Erdmann's Journal fur praktische Chemie
J. Psychol Med	Journal of Psychological Medicine and Mental Pathology
J. Roy Agric Soc.	Journal of the Royal Agricultural Society
J. Roy. Astron Soc Canada	Journal of the Royal Astronomical Society of Canada
J. Roy. Inst Pub Health	Journal of the Royal Institute of Public Health
J. Roy. San Inst	Journal of the Royal Sanitary Institute
J. Roy Soc N S Wales	Journal of the Royal Society of New South Wales
J. Roy. U. S. Inst	Journal Royal United Service Institution
J. Russ Phys Chem Soc.	Journal of the Russian Physical Chemical Society
J. S C. I	Journal of the Society of Chemical Industry
J. Savants	Journal des Savants
J. Sci.	The Journal of Science
J. sci math physi nat.	Journal de ciencias mathematicas, physicas naturales
J. Soc. Arts	Journal of the Royal Society of Arts
J. Soc. Dyers Col.	Journal of the Society of Dyers and Colorists
J. soc. pharm. Anvers	Journal de pharmacie, organe de la société de pharmacie d'Anvers
J. Soc. Electr. Eng.	Journal of the Society of Telegraphic Engineers
J. State Med.	The Journal of State Medicine
J. suisse chim. pharm.	Journal suisse de chimie et pharmacie
J. Travel	The Journal of Travel and Natural History
J. Trop. Med.	The Journal of Tropical Medicine
J. U. S. Artill.	Journal of the United States Artillery
J. Univ. Med.	Journal universel et hebdomadaire de Medecine et de Chirurgie pratiques et des Institutions medicales
J. Univ. Sci. Med.	Journal Universel des Sciences Medicales
J. Wash. Acad. Sci.	Journal of the Washington Academy of Sciences
J. Western Soc. Eng.	Journal of the Western Society of Engineers

Jaarb. Mijnw. Nederl. Ind.	Jaarboek van het Mijnwezen in Nederlandsch Oost-Indie
Jahr. = Jahresbericht	Jahrbuch
Jahr. Agrik.-Chem.	Jahresbericht über die Fortschritte der Agrikulturchemie mit besonderer Berücksichtigung der Pflanz-chemie und Pflanzenphysiologie
Jahr. Berg- u. Huttenw.	Jahrbuch für das Berg- und Huttenwesen im Königreiche Sachsen
Jahr. Kinderheilk.	Jahrbuch für Kinderheilkunde und physische Erziehung
Jahr. Chem.	Jahresbericht der Chemie (Liebig-Kopp)
Jahr. Gahr. Organ.	Jahresbericht über die Fortschritte in der Lehre von den Gährungs-Organismen (Koch)
Jahr. Mineral.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie
Jahr Mineral Beil.-Bd.	Neues Jahrbuch 'für Mineralogie, Geologie, und Palaeontologie, Beilage-Band
Jahr Pharm.	Jahresbericht der Pharmacie
Jahr. Phot.	Jahrbuch der Photographie (Eder)
Jahr. Phot. Reprod.	Jahrbuch für Photographie und Reproduktionstechnik
Jahr. Phy. Ver. Frankfurt	See Frankfurt, Jahr. Phys. Ver.
Jahr. Physiol.	Jahresbericht über die Fortschritte der Physiologie
Jahr. Radioactiv. Electronik.	Jahrbuch der Radioaktivität und Elektronik
Jahr. rein. Chem.	Jahresbericht der reinen Chemie
Jahr. Tier-Chem.	Jahresbericht über die Fortschritte der Tier-Chemie
Jahr wiss. Bot.	Jahrbücher für wissenschaftliche Botanik
Jamaica Inst. J.	Journal of the Institute of Jamaica
Jamaica P.	Jamaica Patent
Jamaica Soc. Arts. Trans.	Transactions of the Jamaica Society of Arts
Jamain, Archives Ophthalm.	Archives d'Ophthalmologie
Jap P.	Japanese Patent
Jardine, Mag. Zool. Bot.	The Magazine of Zoology and Botany
Jena Ann. Acad.	Annales Academiae Jenensis
Jena Ann. Phys. Med.	Die Jenaischen Annalen für Physiologie und Medicin
Jena Ann. Soc. Mineral	Annalen der Societät für die gesammte Mineralogie zu Jena
Jena Denkschr.	Denkschriften der Medicinisch-Naturwissenschaftlichen Gesellschaft zu Jena
Jena Geogr. Ges. Mitth.	Mittheilungen der geographischen Gesellschaft (für Thüringen) zu Jena
Jena Sitzber	Sitzungsberichte der Jenaischen. Gesellschaft für Medicin und Naturwissenschaft
Jena Zts.	Jenaische Zeitschrift für Naturwissenschaft herausgegeben von der Medicinisch-naturwissenschaftlichen Gesellschaft zu Jena
Jern-Kontoret's Ann.	Jern-Kontoret's Annaler
Johns Hopkins Biol. Lab. Mem.	Memoirs from the biological laboratory of the Johns Hopkins University
Johns Hopkins Biol. Lab. Stud.	Johns Hopkins University. Studies from the Biological Laboratory
Johns Hopkins Univ. Circ.	The Johns Hopkins University Circulars
Jura, Trav. Soc. Emul.	Travaux de la Société d'Émulation du Département du Jura
Jurjew	See Dorpat
Just's bot. Jahr.	Just's botanischer Jahresbericht, Leipzig and Berlin
Kali	Kali

Kampen, Mag.	Magazin voor Wetenschappen, Kunsten, &c.
Kan. Acad. Sci. Trans.	Transactions of the . . . annual meeting of the Kansas Academy of Science
Kan. Univ. Quart.	The Kansas University Quarterly
Karlsruhe Bact. Inst. Arb.	Arbeiten aus dem bacteriologischen Institut der technischen Hochschule zu Karlsruhe
Karlsruhe Naturwiss. Ver. Verh.	Verhandlungen des Naturwissenschaftlichen Vereins in Karlsruhe
Kärnten, Berg-Verein, Zts.	Zeitschrift des Berg- u. Hüttenmännischen Vereins für Kärnten
Kärnten Landesmus. Jahr.	Jahrbuch des naturhistorischen Landes-Museums von Kärnten
Kärnten, Zts.	Zeitschrift des berg- und hüttenmännischen Vereines für Kärnten
Karsten	See Botan. Untersuch.
Karsten, Archiv.	Archiv für Mineralogie, Geognosie, Bergbau, und Hüttenkunde
Kassel Ver. Naturk. Ber.	Bericht des Vereins für Naturkunde zu Cassel
Kassel Ver. Naturk. Festschr.	Festschrift des Vereins für Naturkunde zu Cassel zur Feier seines Funfzigjährigen Bestehens
Kastner, Archiv Chem.	Archiv. für Chemie und Meteorologie
Kastner, Archiv. Naturlehre	Archiv für die gesammte Naturlehre
Kazan Soc. Phys.-Math. Bull.	Bulletin de la Société Physico-Mathématique de Kazan
Kazan Soc. Natur. Proc.	Proceedings of the Physico-Mathematical Section of the Society of Naturalists of the Imperial University of Kazan
Kazan Soc. Natur. Trans.	Transactions of the Society of Naturalists of the Imperial University of Kazan
Kazan Univ. Bull.	Bulletin of the Imperial University of Kazan
Kazan Univ. Mem.	Scientific Memoirs of the Imperial University of Kazan
Kekule, Krit. Zts. Chem.	Kritische Zeitschrift für Chemie, Physik, und Mathematik; see also Zts. Chem.
Keram. Rundschau	Keramische Rundschau
Kew Bull.	Royal (Botanic) Gardens, Kew. Bulletin of Miscellaneous Information
Kharkov. Math. Soc. Commun.	Communications de la Société Mathématique de Kharkov
Kiel. Mitth. Ver. Elbe.	Mittheilungen des Vereins nördlich der Elbe zur Verbreitung naturwissenschaftlicher Kenntnisse in Kiel
Kiel, Physiol. Inst. Arb.	Arbeiten aus dem Kieler physiologischen Institut
Kiel, Schr.	Schriften der Universität zu Kiel
Kiel Univ. Mineral. Inst. Mitth.	Mittheilungen aus dem Mineralogischen Institut der Universität Kiel
Kiev Soc. Natur. Mem.	Memoires de la Société des Naturalistes de Kiev
Kjöbenh. Bot. For.	See Bot. Tidsskr.
Kjöbenh. Bot. For. Festskr.	Festschrift, udgivet af den Botaniske Forening i Kjöbenhavn i Anledning af dens Halvhundredaars fest, den 12 April, 1890
Kjöbenh. Bot. For. Medd.	Meddelelser fra den Botaniske Forening i Kjöbenhavn
Kjöbenh. Carlsb. Lab. Medd.	Meddelelser fra Carlsberg Laboratoriet
Kjöbenh. Dansk. Vid. Selsk. Afh.	Det Kongelige Danske Videnskabernes Selskabs naturvidenskabelige og matematiske Afhandlinger

- Kiobenh., Dansk. Vid. Selsk. Skrift. Det Kongelige Danske Videnskabernes Selskabs Skrifter. Naturvidenskabelig og Mathematisk Afdeling
- Kiobenh. Ent. For. See Ent. Medd (Kiobenh.)
- Kiobenh., Oversigt Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger og dets Medlemmers Arbejder i Aaret 1874(-83)...samt. med en Résumé du *Bulletin de l'Académie Royale Danoise des Sciences et des Lettres* pour l'année 1874(-83)
- Kiobenh., Reg Soc. Med Acta. Acta Regiae Societatis Medicae Havniensis
- Kiobenh., Vidensk. Forh. Videnskabelige Forhandlinger ved Siølland Stifts Landemøde
- Kiobenh, Vidensk. Meddel Videnskabelige Meddelelser fra den Naturhistoriske Forening i Kjøbenhavn
- K. K. Ges. Aerzte See Med Jahr
- Klausenburg See Kolozsvár
- Kliniek Kliniek
- Klug, Jahr. Insect. Jahrbücher der Insectenkunde, etc
- Koll Chem. Beihefte Kolloidchemische Beihefte
- Kolloid-Zts Kolloid-Zeitschrift
- Kolozsvár Orvos-Termesz Tars. Ertes. Ertesito a "Kolozsvári Orvos-Termesztudományi Társulat" -nak az . . . orvosi, természetstudományi szaküléséről Proceedings of the Medical and natural history sections of the Klausenburg Medical and Natural History Society
- K Svenska Vet-Akad Kongl Svenska Vetenskaps-Akademiens Handlingar
- Konigsb Archiv. Königsberger Archiv für Naturwissenschaften und Mathematik
- Konigsb Med. Jahr. Königsberger medicinische Jahrbücher; herausgegeben von dem Verein für wissenschaftliche Heilkunde zu Königsberg
- Konigsb Schr. Schriften der physikalisch-ökonomischen Gesellschaft zu Königsberg in Preussen
- Kosmos (Lwow) Kosmos Czasopismo polskiego Towarzystwa przyrodników imienia Kopernika. (Cosmos. The Journal of the Polish Society Naturalists founded in honor of Copernicus)
- Krain Mus'-Ver. Mitth See Laibach, Mus.-Ver. Krain Mitth.
- Krakow Akad. (Mat -Przyrod) Pam. Pamiętnik Akademii Umiejętności w Krakowie. Wydział Matematyczno-Przyrodniczy. (Memoires of the Academy of Science in Cracow. Section of Mathematics and Natural Science)
- Krakow Akad. (Mat -Przyrod) Rozpr. Rozprawy i Sprawozdania z Posiedzeń Wydziału Matematyczno-Przyrodniczego Akademii Umiejętności. (Proceedings of the Section of Mathematics and Natural Science of the Academy of Science)
- Krakow, Akad (Mat -Przyrod) Rozpr. & Spraw. Rozprawy i Sprawozdania z Posiedzeń Wydziału Matematyczno-Przyrodniczego Akademii Umiejętności. (Proceedings of the Section of Mathematics and Natural Science of the Academy of Science)
- Krakow Kom. Fyzyogr Spraw. Akademia Umiejętności w Krakowie. Sprawozdanie Komisji Fyzyograficznej . . . (Academy of Science in Cracow. Report of the Physiographical Commission)
- Krakow, Roczn. Tow. Nauk. Rocznik Towarzystwa Naukowego z Uniwersytetem Jagiellońskim Złączonego
- Krakau, Untersuch. Path Anat. Untersuchungen aus dem Pathologisch-Anatomischen Institute in Krakau

Kreutzer's Jahr. Phot	Kreutzer's Jahresbericht der Photographie
Kristiania, Geogr. Selsk	Det Norske Geografiske Selskabs Arbog
Arb	
Kristiania, Norw Mar.	Report on Norwegian Fishery and Marine Investiga-
Investig. Rep	tions
Kroyer, Naturhist Tidssk	Naturhistorisk Tidsskrift
Kuhn-Archiv.	Kuhn-Archiv (formerly Berichte aus dem physio-
	logischen Laboratorium und der Versuchsanstalt des
	Landwirtschaftlichen Instituts der Universitat Halle
Kult Ing	Der Kultur-Ingenieur (F Dunkelberg)
Kunst	Kunststoffe
Lab Club Trans	Transactions of the Laboratory Club
Laboratory	The Laboratory
Laibach, Jahr Gymnas	Jahresbericht des k k. Ober-Gymnasiums in Laibach
Laibach, Jahr Realschule	Jahresbericht der k k selbstandigen Unter-Realschule
	zu Laibach
Laibach, Jahresh.	Jahresheft des Vereins des Krainischen Landes Mus-
	eums in Laibach
Laibach, Mus-Ver. Krain	Mittheilungen des Muscal-Vereins fur Krain
Mitth	
Lancet	The Lancet, London
Landb Cour	Landbouw-Courant
Landshut Bot. Ver Ber	Bericht des Botanischen Vereines in Landshut
Landw Centr.	Landwirtschaftliches Centralblatt fur Deutschland
Landw Jahr.	Landwirtschaftliche Jahrbucher Zeitschrift fur wis-
	senschaftliche Landwirtschaft und Archiv des
	Koniglich Preussischen Landes-Oekonomie-Kolleg-
	iums
Landw Jahr. Schweiz	Landwirtschaftliches Jahrbuch der Schweiz
Landw Presse	Landwirtschaftliche Presse
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen
Landw Ztg	Landwirtschaftliche Zeitung
Laon, Soc Acad Bull.	Bulletin de la Société Academique de Laon
Laurent Ann Anat.	Annales Francaises et Etrangères d'Anatomie et de
	Physiologie, appliquees a la Medecine et a l'Histoire
	Naturelle
Laurent Gerhardt, Compt	Comptes rendus Mensuels des Travaux Chimiques
rend.	
Lausanne, Bull Soc Med	Bulletin de la Société Medicale de la Suisse Romande
Lausanne, Bull Soc Vaud.	Bulletin des Séances de la Société Vaudoise des Sciences
	Naturelles
Lausitz Monatschr.	Lausitzische (und neue Lausitzische) Monatschrift
	Organ der Oberlausitzischen Gesellschaft der Wissen-
	schaften
Leather	Leather
Leather Mfr.	Leather Manufacturer
Leather Tr. Rev	Leather Trades Review
Leather World	Leather World, The
Lederind.	Lederindustrie (Deutsche Gerber-Zeitung)
Ledermarkt	Ledermarkt, Der (See also Collegium)
Leeds, Trans Phil Soc	Transactions of the Philosophical and Literary So-
	cietv of Leeds
Leicester, Lit. Phil Soc	Selection of Papers, of the Literary and Philo-
Selection	sophical Society of Leicester
Leicester Soc. Rep.	Leicester Literary and Philosophical Society .. Re-
	port of the Council
Leicester Soc Trans.	Transactions of the Leicester Literary and Philo-
	sophical Society

- Leide See Leyden  
 Leiden, Ann. Acad. Annales Academiae Lugduno-Batavae  
 Leiden, Tijdschr. Entom. Tijdschrift voor Entomologie  
 Leipzig, Abh. Jablon. Ges. Abhandlungen bei Begründung der k. Sachsichen Gesellschaft der Wissenschaften am Tage der zweihundertjährigen Geburtsfeier Leibnizens  
 Leipzig, Abh. Math. Phys. Abhandlungen der Mathematisch-Physischen Classe der Königlich Sachsichen Gesellschaft der Wissenschaften  
 Leipzig, Arbeit. Physiol. Arbeiten aus der physiologischen Anstalt zu Leipzig  
 Anst.  
 Leipzig, Astron. Ges. Vierteljahrsschrift der Astronomischen Gesellschaft  
 Vier-  
 telj.  
 Leipzig, Ber. Math. Phys. Berichte über die Verhandlungen (Math. Phys. Classe) der Königlich Sachsichen Gesellschaft der Wissenschaften zu Leipzig  
 Leipz. Farb. Ztg. Leipziger Farber- und Zeugdrucker-Zeitung  
 Leipzig Jablon. Preisschr. Preisschriften gekrönt und herausgegeben von der fürstlich Jablonowski'schen Gesellschaft zu Leipzig  
 Leipzig, Monatschr. Text. Leipziger Monatsschrift für Textil-Industrie  
 Ind.  
 Leipzig, Naturf. Ges. Sitzungsberichte der Naturforschenden Gesellschaft zu Leipzig  
 Sitz-  
 ber  
 Leipzig, Physiol. Anst. Arbeiten aus der Physiologischen Anstalt zu Leipzig  
 Arb.  
 Leipzig, Schr. Naturf. Ges. Schriften der Naturforschenden Gesellschaft zu Leipzig  
 Leipzig, Verh. Med. Ges. Verhandlungen der Medicinischen Gesellschaft  
 Leyden Mus. Notes Notes from the Leyden Museum  
 Leo, Mag. Magazin für Heilkunde und Naturwissenschaft in Pohlen  
 Leoben, Berg. u. Hutt. Berg- und Huttenmannisches Jahrbuch der k. k. Montan Lehranstalten zu Leoben und Pribram  
 Jahr.  
 Leonhard Bronn See Neues Jahr. Mineral  
 Leonhard Bronn, Jahr. Jahrbuch für Mineralogie, Geognosie, Geologie, und Petrefaktenkunde  
 Leonhard Bronn, Neu. Neues Jahrbuch für Mineralogie, Geognosie, Geologie und Petrefaktenkunde  
 Jahr.  
 Leonhard, Taschenbuch Taschenbuch für die gesamte Mineralogie  
 Leonhard, Zts. Zeitschrift für Mineralogie  
 Leopold.-Carol. Deutsch. See Ac. Nat. Curios. Nova Acta Leopoldina  
 Akad. Naturf.  
 Leopoldina Leopoldina. Amtliches Organ der Kaiserlichen Leopoldino-Carolinischen Deutschen Akademie der Naturforscher  
 Letters on Brewing Letters on Brewing  
 Les Mondes Revue hebdomadaire des Sciences et de leurs applications  
 Licht. Licht: Zeitschrift für Photographie herausgegeben vom Photographischen Verein. zur Berlin  
 Liege, Ann. Acad. Annales Academiae Leodiensis  
 Liege Assoc. Ingen. Annu. See Rev. Univ. Mines  
 Liege, Mem. Soc. Emul. Memoires de la Société Libre d'Émulation de Liege  
 Liege, Mem. Soc. Sci. Memoires de la Société (Royale) des Sciences de l'Agriculture, et des Arts à Liege  
 Liege Lab. Fredericq Trav. Université de Liege. Institut de Physiologie. Travaux du Laboratoire de Leon Fredericq  
 Lille Inst. Zool. Trav. Travaux de l'Institut Zoologique de Lille et du Laboratoire de Zoologie Maritime de Wimereux (Pas-de-Calais). Travaux de la Station Zoologique de Wimereux

Lille Mem. Soc.	Memoires de la Société (Imperiale) des Sciences, de l'Agriculture et des Arts de Lille
Lille, Mem Soc. Sci.	Memoires de la Société (Royale) des Sciences, etc., a Lille
Lille, Seances Publ.	Seances Publiques de la Société des Amateurs
Lille, Trav.	Recueil des Travaux de la Société d'Amateurs des Sciences, de l'Agriculture, et des Arts a Lille
Lille, Trav Mem.	Travaux et Memoires de l'Universite de Lille
Lima, Mem Cien Nat.	Memorias de Ciencias Naturales y de Industrial (Lima)
Limbourg, Soc Sci. Bull.	Bulletin de la Société Scientifique et Litteraire du Limbourg
Limoges, Assises	Assises scientifiques de Limoges (Institut des Provinces de France)
Lindblom, Bot Notiser	Botaniska Notiser
Linn	Linnaea ein Journal fur die Botanik
Linn Entom.	Linnaea Entomologica
Linn Soc. J.	The Journal of the Linnean Society. Botany and Zoology
Linn Soc. Trans.	The Transactions of the Linnean Society of London
Linn Soc Proc	Proceedings of the Linnean Society of London
Linneska Samf Handl.	Linneska Samfundets Handlingar for ar 1832
Linz, Ber.	Bericht uber das Museum Francisco-Carolinum in Linz
Lisboa, Acad Sci Mem.	Historia e Memorias da Academia Real das Sciencias de Lisboa
Lisboa, Actas	Actas das Sessoes da Academia Real das Sciencias de Lisboa
Lisboa, Ann	Annaes das Sciencias e Lettras
Lisboa, J. Math Sci	Jornal de Sciencias Mathematicas, Physicas e Naturaes publicado sob os Auspicios da Academia Real das Sciencias de Lisboa
Litterar Annal	Litterarische Annalen der gesammten Heilkunde
Liverpool Biol Soc. Proc	Proceedings and Transactions of the Liverpool Biological Society
Liverpool, Lit. Phil Soc Proc.	Proceedings of the Literary and Philosophical Society of Liverpool
Liverpool Mar. Biol Comm	See Liverpool Biol Soc Proc ; Liverpool Biol Soc. Proc & Trans , Liverpool Lit Phil. Soc Proc
Liverpool Med Chir J	Liverpool Medico-Chirurgical Journal
Liverpool School Trop Med Mem	Liverpool School of Tropical Medicine. Memoirs
Liverpool. Thompson Yates Lab. Rep	The Thompson Yates Laboratories Report
Loc. Gov Bd Rep (Med Off.)	. Annual Report of the Local Government Board Supplement containing the Reports of the Medical Officer
London	See Int Congr Hyg Trans, 1891, Int Congr Zool Proc. 1898
London, Ann Med Surg	Annals of Medicine and Surgery, Records of the occurring Improvements, &c
London, Cryst Soc Proc	Proceedings of the Crystallological Society
London Elec Soc Proc.	Proceedings of the London Electrical Society
London, Fed. Inst. Brew- ing J.	Journal of the Federated Institutes of Brewing containing the Transactions of the various Institutes
London J. Med.	London Journal of Medicine
London, Med. Phys J.	The Medical and Physical Journal
London, Med. Soc. Trans	Transactions of the Medical Society of London

London, Obstet. Soc. Trans.	Transactions of the Obstetrical Society of London
London, Odont. Soc. Trans.	Transactions of the Odontological Society of London
London Path. Soc. Trans.	Transactions of the Pathological Society of London
Lond. Phot. Soc.	London Photographic Society
London Phys. Soc. Proc.	Proceedings of the Physical Society of London
London Physiol. J.	London Physiological Journal
London Poly. Rev.	The London Polytechnic Review and Magazine
London, Poly. Mag.	Polytechnic Magazine and Journal of Science, Letters, and Fine Arts
London, Sci. Soc. Proc.	Proceedings of the Scientific Society of London
London, Soc. Imp. Med. Trans.	Transactions of the Society for the Improvement of Medical and Chirurgical Knowledge
Lotos	Lotos, Jahrbuch für Naturwissenschaft im Auftrage der Vereines "Lotos"
Lousiana Planter	Louisiana Planter and Sugar Manufacturer, The
Louvaine, Ann. Acad.	Annales Academiae Lovaniensis
Lowell Obs. Ann.	Annals of the Lowell Observatory
Lucca, Atti Accad.	Atti della R. Accademia Lucchese di Scienze, Lettere, et Arti
Lumière	La Lumière; Revue de la Photographie
Lumière elec	Lumière électrique, La
Lund, Acta Univ.	Acta Universitatis Lundensis Lunds Universitets Ars-skrift. Afdelningen för Matematik och Naturvetenskap
Lund Bot. För.	See Bot. Centrbl.; Bot. Notiser
Lund, Phys Sällsk Tidskr	Physiografiska Sällskapets Tidskrift
Luneb, Denkschr.	Denkschriften des naturwissenschaftlichen Vereins für das Fürstenthum Luneburg
Luneb, Jahr. Naturwiss. Ver.	Jahresbericht über die Thatigkeit des naturwissenschaftlichen Vereins in Luneburg
Luneb. Jheft. Naturwiss. Ver.	Jahreshefte des Naturwissenschaftlichen Vereins für das Fürstenthum Luneburg
Luxemb, Inst. Roy. Publ.	Publications de l'Institut Royal Grand-Ducal de Luxembourg Section des Sciences Naturelles
Luxemb. P.	Luxembourg Patent
Luxemb. Soc. Bot. Rec. Mem Trav.	Recueil des Memoires et des Travaux publies par la Société Botanique du Grant-Duche de Luxembourg
Luxemb. Soc. Sci Natur.	Société des Sciences Naturelles du Grand-Duche de Luxembourg
Lyon	Lyon scientifique et industriel
Lyon, Acad. Sci. Mem.	Memoires de l'Academie des Sciences, Belles-Lettres, et Arts de Lyon
Lyon Mus. Hist. Natur. Archiv.	Archives du Museum d'Histoire naturelle de Lyon
Lyon Soc. Agric Ann	Annales de la Société d'Agriculture, Histoire naturelle et Arts utiles de Lyon. Annales de la Société d'Agriculture, Sciences et Industrie de Lyon
Lyon Soc. Bot. Ann.	Annales de la Société Botanique de Lyon
Lyon, Soc. Linn. Ann.	Annales de Société Linneenne de la Lyon
Lyon, Soc. Linn. Compt. rend.	Comptes Rendus des Travaux de la Société de Medecine
Lyon, Soc. Sci. Med. Mem.	Memoires et Comptes-Rendus de la Société des Sciences Medicales de Lyon
Lyon Univ. Ann.	Annales de l'Universite de Lyon
Maandbl. Natuurweten.	Maandblad voor Natuurwetenschappen, uitgegeven door de Sectie voor Natuurwetenschappen van het Genootschap ter Bevordering van Natuur-, Genees- en Heelkunde te Amsterdam



Maclurian Lyceum, Contrib.	Contributions of the Maclurian Lyceum to the Arts and Sciences
Macon Acad Ann.	Annales de l'Academie de Macon Société des Arts, Sciences, Belles-Lettres et (d')Agriculture (de Saone-et-Loire)
Macon, Soc. Agric Compt. rend.	Comptes Rendus des Travaux de la Société d'Agriculture Sciences, et Belles-Lettres
Macon Soc Compt rend.	Compte Rendu des Travaux de la Société (d'Agriculture), des Sciences, Arts et Belles-lettres, de Macon
Madras J	The Madras Journal of Literature and Science
Madras Quart J.	Madras Quarterly Journal of Medical Science
Madrid	See Congr. Int Hig Act 1898
Madrid Acad Cien. Mem.	Memoires de la Real Academia de Ciencias Exactas, Fisicas y Naturales de Madrid
Madrid, Anales Hist. Natur	Anales de Historia Natural
Madrid, Anales Minas	Anales de Minas
Madrid, Anuar.	Anuario del Real Observatorio de Madrid
Madrid, Bol	Boletin Oficial del Ministerio de Comercio
Madrid, Ingen Ind Anales	Anales de la Asociacion de Ingenieros Industriales
Madrid, Mem.	Memorias de la Real Academia de Ciencias
Madrid, Revista	Revista de los Progresos de las Ciencias exactas, fisicas, y naturales
Madrid, Soc. Hist. Natur. Anales	Anales de la Sociedad Espanola de Historia Natural
Mag. Gesammt. Thierheilk.	Magazin fur die gesammte Thierheilkunde
Mag. Natur. Hist.	The Magazine of Natural History, and Journal of Zoology, Botany, Mineralogy, Geology, and Meteorology
Mag. Natur. Phil.	The Magazine of Natural Philosophy
Mag. Naturvid.	Magazin for Naturvidenskaberne
Mag. Zool	Magasin de Zoologie
Magdeb. V. Ver. Abh. Naturwiss	Abhandlungen des Naturwissenschaftlichen Vereins zu Magdeburg
Magdeb. V. Ver. Festschr. Naturwiss.	Festschrift zur Feier des 25 jahrigen Stiftungstages des Naturwissenschaftlichen Vereins zu Magdeburg
Magdeb. V. Ver. Jahr. Abh. Naturwiss.	Jahresbericht und Abhandlungen des naturwissenschaftlichen Vereins in Magdeburg.
Magendie, J. Physiol	Journal de Physiologie, experimentale et pathologique
Magyar Akad. Ertes. (Math. Termesz.)	Magyar Akademiai Ertesito A matematikai, es Termeszettudományi osztályok közlönye. (Report of the Hungarian Academy. Communications of the Mathematical and Natural Science Sections)
Magyar Boripar	Magyar Boripar
Magyar Nemzeti Muzeum	See Termr. Fuz.
Magyar Term. Tars.	See Term. Közlön.
Magyar Tud. Akad. Ertes.	A Magyar Tudományos Akademia Ertesitoje. (Report of the Hungarian Academy of Science)
	Akademiai Ertesito a Magyar Tud Akademia Megbizasabol. (Report by the Committee of the Hungarian Academy of Science)
Magyar Tud. Akad. Ertek. (Math.)	Ertekezések a Matematikai Tudományok köréből. Kiadja a Magyar Tudományos Akademia. (Memoirs in the Mathematical Sciences. Published by the Hungarian Academy of Science)

Magyar Tud. Akad. Ertek. (Termt.)	Ertekezések a Természettudományok köréből. Kiadja a Magyar Tudományos Akadémia. (Memoirs in the Natural Sciences. Published by the Hungarian Academy of Science)
Magyar Tud Akad Evk.	A Magyar Tudományok Akadémia Évkönyvei (Annals of the Hungarian Academy of Science)
Maine Loire Soc. Mem. Acad.	Memoires de la Société Académique de Maine et Loire
Majocchi, Ann Fis. Chim.	Annali di Fisica, Chimica, etc.
Malpighia	Malpighia Rassegna mensile di Botanica
Malta P.	Malta Patent
Malvern Field Club Trans	The Transactions of the Malvern Naturalists' Club
Manufact. and Build	The Manufacturer and Builder
Manchester, Engin. Proc.	Proceedings of the Manchester Institution of Engi- neers
Manchester, Lit Phil Soc. Mem.	Memoirs of the Literary and Philosophical Society of Manchester
Manchester, Lit. Phil Soc Proc.	Proceedings of the Literary and Philosophical Society of Manchester
Manchester Micro. Soc. Trans.	Manchester Microscopical Society. Transactions and Annual Report
Manchester, Owens Coll. Biol. Lab Stud.	Studies from the Biological Laboratories of the Owens College
Manchester, Owens Coll. Stud. Biol.	Studies in Biology from the Biological Department of the Owens College
Mannheim, Jahr.	Jahresbericht des Mannheimer Vereins für Natur- kunde
Mans, Soc. Agric Bull.	Bulletin de la Société d'Agriculture, etc., de la Sarthe
Mans, Soc. Bull.	Bulletin de la Société (Royale) d'Agriculture, Sciences et Arts du Mans
Mans, Soc. Roy. Trav.	Analyse des Travaux de la Société (Royale) des Arts du Mans
Marburg, Ges. Naturwiss. Schr.	Schriften der Gesellschaft zur Beförderung der gesammten Naturwissenschaften zu Marburg
Marianini	See Mem. Fis Sperim.
Marne, Soc. Agric Compte Annuel	Compte annuel et Sommaire des Travaux de la Société Agricole, etc., du département de la Marne
Marne, Soc. Agric. Seance	Seance publique de la Société d'Agriculture, etc., du département de la Marne
Marseille, Ann. Sci.	Annales de Sciences et de l'Industrie du midi de la France
Marseille Fac. Sci Ann.	Annales de la Faculté des Sciences de Marseille
Marseille Lab. Zool. Mar. Trav.	See Marseille Mus. Ann.
Marseille, Mem. Acad	Memoires publiés par l'Académie de Marseille
Marseille, Mem. Soc. Emul.	Memoires de la Société d'Émulation de la Provence
Marseille Mus. Ann.	Annales du Musée d'Histoire naturelle de Marseille
Maschin.-Constr.	Der praktische Maschinen-Construkteur (W. Uhland)
Maschinenb.	Der Maschinenbauer
Mass. Bd. Health Report	Annual Report of the State Board of Health, Lunacy and Charity of Massachusetts. Annual Report of the State Board of Health of Massachusetts
Mass Insects Report	.. Annual Report on the Injurious and Beneficial In- sects of Massachusetts
Mass. Med. Soc. Commun.	Massachusetts Medical Society's Communications
Mat. grasses	Le Matieres grasses
Maurice, Soc. Hist. Natur. Rapp.	Septieme Rapport Annuel sur les Travaux de la Société d'Histoire Naturelle de l'Île Maurice

Mauritius, Meteorol. Soc. Proc	Proceedings, &c, of the Meteorological Society of Mauritius
Mauritius, Meteorol. Soc. Trans.	Transactions of the Meteorological Society of Mauritius
Mauritius P.	Mauritius Patent
Mauritius Roy. Soc. Trans	Transactions de la Société Royale des Arts et des Sciences de Maurice
Meaux, Bull Soc. Archeol.	Bulletin de la Société d'Archeologie, Sciences, Lettres et Arts du dept de Seine et Marne
Mechan. Engin. Inst Proc	Institution of Mechanical Engineers Proceedings
Meckel, Archiv	Archiv für Anatomie und Physiologie
Meckel, Deut Archiv	Deutsches Archiv für die Physiologie
Med Assoc J.	Journal edited for the Provincial Medical and Surgical Association
Med Bot Soc Trans	Transactions of the Medico-Botanical Society of London
Med. Chem Unters	Medicisch-chemische Untersuchungen, aus dem Laboratorium für angewandte Chemie zu Tübingen
Med. Chir Soc Proc	Proceedings of the Royal Medical and Chirurgical Society of London
Med -Chir. Trans	Medico-Chirurgical Transactions
Med Chir. Ztg.	Medicisch-chirurgische Zeitung
Med Congr.	See Congr Int Med C R, Congr Int Sci Med. C T, Congr Med Int Atti, Int. Med Congr. Trans, Int. Med Congr. Verh
Med Jahr.	Medizinische Jahrbücher, von der K. K. Gesellschaft in Wien
Med Klinik.	Medizinische Klinik
Med. naturwiss. Archiv	Medizinisch-naturwissenschaftliches Archiv.
Med. Off. India Sci. Mem.	Scientific Memoirs by Medical Officers of the Army of India
Med Phys J.	The Medical and Physical Journal
Med. Rec.	The Medical Record, N. Y.
Med. Times	The Medical Times, London
Med. Trans.	Medical Transactions
Med. Wochenschr.	Medizinische Wochenschrift
Med Ztg. Russ	Medicische Zeitung Russlands
Medd. Gronland	Meddelelser om Gronland
Medd. K. Vetenskapsakad. Nobel-inst.	Meddelanden från K. Vetenskapsakademiens Nobel-institut
Meisner, Ann.	Annalen der allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften
Meisner, Anzeiger	Naturwissenschaftlicher Anzeiger der Allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften
Melbourne	See Victoria
Mem. accad. Lincei	Memorie della r. accademia dei Lincei, Classe di scienze fisiche, matematiche e naturali
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino
Mem. Chem. Soc.	Memoirs and proceedings of the Chemical Society of London prior to 1848
Mem. Coll. Sci. Eng. Kyoto	Memoirs of the College of Science and Engineering, Kyoto Imperial University
Mem. Fis. Sperim.	Memorie di Fisica sperimentale
Mem. Imp. Mineral. Soc. Petrograd	Memoirs of the Imperial Mineralogical Society of Petrograd
Mem. Lepidopt., St. Petersb.	Memoires sur les Lepidopteres

Mem. Manch. Lit. Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society
Mem. Med. Milit.	Recueil de Memoires de Medecine, de Chirurgie et de Pharmacie Militaires
Mem poud salp	Memorial des poudres et salpetres
Mem rev. soc. cien "Antonio Alzate"	Memorias y revista de la sociedad cientifica "Antonio Alzate"
Mem. Soc. Ing. civ	Memoires et Compte-Rendu des travaux de la Société des Ingenieurs Civils, etc.
Mem Soc. Nat. Kiev	Memoirs of the Society Nat. Kiev.
Mem. Valdarnesi	Memorie Valdarnesi
Mende, Soc. Agric. Bull.	Bulletin de la Société d'Agriculture, Industrie, Sciences, et Arts de departement de la Lozere
Mende, Soc Agric Mem	Memoires et Analyses des Travaux de la Société d'Agriculture, Commerce, Sciences, et Arts de la ville de Mende, departement de la Lozere
Merck's Ann Rep	Merck's Annual Report
Merck's Archiv.	Merck's Archives, New York
Messenger Math	The Messenger of Mathematics
Met.	Metallurgical-Metallurgia
Met. Chem Eng	Metallurgical and Chemical Engineering
Met. ital.	Metallurgia italiana, La
Met. Rev	The Metallurgical Review
Metal Ind.	The Metal Industry
Metal Tech.	Metal Technik
Metall Ind Ztg	Deutsche Metall-Industrie-Zeitung
Metallarb	Der Metallarbeiter
Metallurgie	Metallurgie
Metaxa, Ann Med. Chir	Annali medico-chirurgici.
Metz Acad. Mem	Memoires de l'Academie (Imperiale) de Metz
Metz, Assises	Assises scientifiques de Metz (Institut des Provinces de France)
Metz, Seance Gen.	Société des Lettres, Sciences, Arts, et Agriculture de Metz
Metz Soc. Hist. Natur Bull.	Bulletin de la Société d'Histoire naturelle de Metz
Mex.	Mexican, Mexico, Mexicane
Mex. P	Mexican Patent
Mex. Mus Anales	Anales del Museo Nacional de Mexico
Mex. Registro Trim.	Registro trimestre, o Coleccion de Memorias de Historia, Literatura, Ciencias, etc, por una Sociedad de Literatos
Mex. Soc. "Alzate" Mem.	Memorias de la Sociedad Cientifica "Antonio Alzate"
Mexique Archiv. Comm. Sci.	Archives de la Commission Scientifique du Mexique, publiees sous les auspices du Ministere de l'Instruction Publique
Meyer Bros Drug.	Meyer Brothers Druggist, St. Louis
Meyer Jahr. Chem.	R. Meyer's Jahrbuch der Chemie
Michigan, Fish Comm Report	Biennial Report of the State Board of Fish Commissioners. (Contains the Michigan Fish Comm. Bull.)
Micro. J.	Quarterly Journal of Microscopical Science
Micro Soc. J.	Journal of the Royal Microscopical Society
Micro. Soc. Trans.	Transactions of the Microscopical Society of London
Midl. Drug.	Midland Druggist and Pharmaceutical Review
Midl. Med. Surg. Rep.	Midland Medical and Surgical Reporter
Midl. Quart. J. Med. Sci.	The Midland Quarterly Journal of Medical Sciences
Milano, Ann. Scienz.	Annali di Scienze e Lettere

Milano, Atti Ginnas.	Atti dell' I. R. Ginnasio Liceale Convitto Longone in Milano
Milano, Atti Ist. Lomb	Atti dell' I R Istituto Lombardo di Scienze, Lettere, ed Arti
Milano, Atti Soc Ital	Atti della Societa Italiana di Scienze Naturali
Milano, Cagnola Atti	Atti della Fondazione Scientifica Cagnola dalla sua istituzione in poi
Milano, Giorn Soc Incor.	Giornale della Societa d'Incoraggiamento delle Scienze, etc, stabilita in Milano
Milano, Ist. Lomb. Adunanze	Solenni Adunanze del R Istituto Lombardo di Scienze e Lettere
Milano, Ist. Lomb. Rapporti	Rapporti sui Progressi delle Scienze del R. Istituto Lombardo di Scienze
Milano, Ist Lomb Rend	Rendiconti dell' Istituto Lombardo di Scienze e Lettere —Classe di Scienze matematiche e naturali
Milano, Mem Ist Lomb	Memorie dell' I R. Istituto Lombardo di Scienze, etc.
Milano, Mem Ist Lomb Veneto	Memorie dell' I R Istituto del regno Lombardo-Veneto
Milch Zentr	Milchwirtschaftliches Zentralblatt
Milch Ztg.	Milch Zeitung
Min Eng. World	Mining and Engineering World
Min. J.	The Mining Journal
Min Rev.	Mining Review, a Monthly Record of Geology
Min Sci.	Mining Science
Min Sci Press	Mining and Scientific Press
Min Smelt Mag	The Mining and Smelting Magazine, a monthly review of Practical Mining, Quarrying, and Metallurgy
Min Soc J.	See Min Mag
Mineral. Mag.	The Mineralogical Magazine and Journal of the Mineralogical Society of Great Britain and Ireland
Mineral Mitth	Mineralogische Mittheilungen
Mineral Petr. Mitth	(Tschermak's) Mineralogische und Petrographische Mittheilungen
Mines and Minerals	Mines and Minerals
Minn Acad. Sci. Bull	Bulletins of the Minnesota Academy of Natural Sciences
Minn Acad Sci Pap	The Minnesota Academy of Natural Sciences at Minneapolis, Minn Occasional Papers
Minn. Bot. Stud	Geological and Natural History Survey of Minnesota. Minnesota Botanical Studies
Miquel, Bull.	Bulletin des Sciences Physiques et Naturelles en Neerlande
Misc. Ent.	Miscellanea Entomologica
Mitau, Quatember	Die Quatember
Mitth. Artill. Geniew.	Mittheilungen über Gegenstände des Artillerie- und Genie-wesens
Mitth. Bohmen. Archit Ing. Ver.	Mittheilungen des Architekten und Ingenieur Vereins im Königreiche Bohmen
Mitth. Centralst. Wiss - tech. Unters.	Mittheilungen aus der Centralstelle für wissenschaftlich-technische Untersuchungen
Mitth. Gewerbever. Nassau	Mittheilungen für den Gewerbeverein für Nassau
Mitth. Kais. Gesundhts.	Mittheilungen aus dem Kaiserlichen Gesundheitsamte, Berlin
Mitth. Königl. Materialprüfungsamt	Mittheilungen aus dem Königlichen Material prüfungsamt zu Gross Lichterfelde West
Mitth. Hannov. Gewerbever.	Mittheilungen des Gewerbevereins für Hannover

Mitth. Lebensm. Hyg.	Mittheilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene veröffentlicht vom Schweizer Gesundheitsamt
Mitth. Malerei	Technische Mittheilungen für Malerei
Mitth. könig. Prüfungsans. Wasser-versorgung	Mittheilungen aus der königlichen Prüfungsanstalt für Wasser-versorgung und Abwasser beseitigung zu Berlin
Mitth. Tech. Gew. Mus.	Mittheilungen aus dem Technischen Gewerbe Museum
Mitth. Techn. Versuchsamtes	Mittheilungen des k. k. Technischen Versuchsamtes
Mitth. Zool. Sta. Neapel	Mittheilungen aus der zoologischen Station zu Neapel. etc
Mo. Insects Report	Annual Report on the Noxious, Beneficial and other Insects, of the State of Missouri, made to the State Board of Agriculture
Mod. Sugar Planter	Model Sugar Planter, The
Modena, Accad. Sci. Mem.	Memorie della Regia Accademia di Scienze, Lettere ed Arti di Modena
Modena, Annu. Soc. Natur.	Annuario della Società dei Naturalisti in Modena
Modena Atti Soc. Natur.	Atti della Società dei Naturalisti di Modena
Modena, Mem. Soc. Ital.	Memorie di Matematica e di Fisica della Società Italiana delle Scienze
Modena, Relazione	Relazione delle Adunanze della R. Accademia di Scienze, Lettere, ed Arti di Modena, nell' Anno Accademico 1842-43
Moigno, Annu. Cosmos	Annuaire du Cosmos
Mois chim. electrochim.	Mois chimique et electrochimique, Le
Mois min. met.	Mois minier et metallurgique, Le
Mois sci. ind.	Mois scientifique et industriel, Le
Moleschott, Unters.	Untersuchungen zur Naturlehre des Menschen und der Thiere
Moll, Ann.	Annalen der Berg- und Huttenkunde
Moll, Efemeriden	Efemeriden der Berg- und Huttenkunde
Moll, Jahr. Berg.	Jahrbücher der Berg- und Huttenkunde
Moll, Neue Jahr.	Neue Jahrbücher der Berg- und Huttenkunde
Mon. ceram. verr.	Moniteur de la ceramique de la verrerie et journal du ceramiste et du chauxfourneur (reains)
Mon. cord.	Moniteur de la cordonnerie
Mon. fils tiss.	Moniteur des fils et tissus
Mon. Ind.	Moniteur Industriel
Mon. Ind. Belge	Moniteur Industriel Belge
Mon. Pap.	Moniteur Papeterie
Mon. Sci.	Moniteur Scientifique (Quesneville)
Mon. teint.	Moniteur de la teinture des apprêts et de l'impression des tissus
Monats.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften Gesammelte Abhandlungen aus den Sitzungsberichten der kaiserlichen Akademie der Wissenschaften
Monats. Dermatol.	Monatshefte für praktische Dermatologie
Monatsbl. Hannover Gewerbever.	Monatsblatt des Gewerbevereins für Hannover
Monatschr. Text.-Ind.	Leipziger Monatsschrift für Textil-Industrie
Monatschr. Zahn	Monatsschrift für Zahnärzte
Montevideo Mus. Nac. Anales	Anales del Museo Nacional de Montevideo
Monthly Amer. J. Geol.	The monthly Journal of Geology and Natural Science
Monthly Archiv. Med. Sci.	Monthly Archives of the Medical Sciences

Monthly Cons. & Trade Report	The monthly Consular and Trade Reports
Montpellier, Acad. Proces-Verb.	Extraits des Proces-Verbaux des Seances de l'Academie des Sciences et Lettres
Montpellier, Acad. Sci. Mem.	Academie des Sciences et Lettres de Montpellier
Montpellier Inst. Zool. Trav.	Travaux originaux du Laboratoire Zoolique de la Faculte des Sciences de Montpellier et de la Station Maritime de Cette
Montpellier, Mem. Acad. Sect. Med.	Memoires de l'Academie des Sciences et Lettres Section de la Medecine
Montpellier, Recueil. Bull.	Recueil des Bulletins publies par la Société Libre des Sciences, etc.
Montreal Natur. Hist. Soc. Proc.	See Canad. Rec. Sci.
Montreal Pharm. J.	Montreal Pharmaceutical Journal
Montsouris	See under Paris
Morphol. Arb.	Morphologische Arbeiten
Morphol. Jahr.	Morphologisches Jahrbuch
Moscou	See Congr Int Anthropol. C. R 1892, Congr Int Med C. R 1897, Congr Int Zool (C. R.) 1892
Moscou, Comment. Soc. Phys. Med.	Commentationes Societatis Physico-Medicae apud Universitatem Mosquensem institutae
Moscou, Soc. Natur. Bull.	Bulletin de la Société Imperiale des Naturalistes
Moscou, Soc. Natur. Mem.	Memoires de la Société Imperiale des Naturalistes de Moscou
Moscou, Soc. Natur. Nouv. Mem.	Nouveaux Memoires de la Société Imperiale des Naturalistes de Moscou
Moscow Soc. Sci. Bull.	Bulletin of the Imperial Society of Lovers of Natural Science, Anthropology and Ethnography, in connection with the Imperial University of Moscow
Moscow Univ. Mem (Natur. Hist.)	Scientific Memoirs of the Imperial University of Moscow. Natural History Section
Moscow Univ. Mem. (Phys. Math.)	Scientific Memoirs of the Imperial University of Moscow Physico-Mathematical Section
Moselle, Bull. Soc. Hist. Natur.	Bulletin de la Société d'Histoire Naturelle du departement de la Moselle
Moselle, Trav. Soc. Sci. Med.	Expose des Travaux de la Société des Sciences Medicales de la Moselle
Mov. Pict. World	Moving Picture World
Mulder, Archief.	Natuur- en Scheikundig Archief.
Mulder, Scheik. Verh.	Scheikundige Verhandelingen en Onderzoekingen
Müller, Archiv.	Archiv. für Anatomie, Physiologie, und wissenschaftliche Medicin.
München, Akad. Abh.	Abhandlungen der Mathematisch-Physikalischen Classe der königlich Bayerischen Akademie der Wissenschaften
München, Akad. Sitzber.	Sitzungsberichte der Mathematisch-Physikalischen Classe der k. B. Akademie der Wissenschaften München
München Bot. Ver.	See Bot. Centrbl.
München, Bull. Akad.	Bulletin der k. Akademie der Wissenschaften
München, Denkschr.	Denkschriften der Königl. Baierschen Akademie der Wissenschaften zu München
München, Entom. Ver. Mitth.	Mittheilungen des Münchener Entomologischen Vereins
München, Gelehrte Anz.	Gelehrte Anzeigen

München Ges. Morphol. Physiol. Sitzber.	Sitzungsberichte der Gesellschaft für Morphologie und Physiologie in München
München, Naturwiss. Tech. Comm. Abh	Abhandlungen der naturwissenschaftlich-technischen Commission bei der Königl. Baierischen Akademie
München Phot. Ges.	See Wien, Photogr. Correspond.
München, Sitzber.	Sitzungsberichte der Königl. Baierischen Akademie der Wissenschaften zu München
München Thierarznei-Schule Jahr.	Jahresbericht der k. Central-Thierarznei-Schule in München
München Thierärztl. Hochschule Jahr.	Jahresbericht der k. Thierärztlichen Hochschule in München
München, Zts. Archit.	Zeitschrift des Bayerischen Architekten- und Ingenieur-Vereins
Munic. Engin.	Municipal Engineer
Munic. J. Engin.	Municipal Journal and Engineer
Munster, Abh. Aerzt. Ges.	Abhandlungen und Beobachtungen der ärztlichen Gesellschaft zu Munster
Museum Senckenb.	Museum Senckenbergianum
Must Ztg.	Leipziger Farber Zeitung (Farberei-Musterzeitung)
N. Brunsw. Natur. Hist. Soc. Bull.	Bulletin of the Natural History Society of New Brunswick
N. England Bot. Club	See Rhodora
N. Engl. Eng.	New England Engineer, The
N. England J. Med.	New England Journal of Medicine and Surgery.
N. Erf. Erfahr.	Neueste Erfindungen und Erfahrungen
N. Hampshire San. Bull.	New Hampshire Sanitary Bulletin
N. Haven	See Connecticut
N. Idea	New Idea (The), Detroit
N. Med. Phys. J.	New Medical and Physical Journal
N. Mex. Agric. Coll. Bull.	New Mexico Agricultural College Experiment Station. Las Cruces, N. M. Bulletin. New Mexico College of Agriculture and the Mechanic Arts Agricultural Experimental Station Bulletin
N. Orleans Med. Surg. J.	New Orleans Medical and Surgical Journal
N. Orleans Proc.	Proceedings of the New Orleans Academy of Sciences
N. Russ. Soc. Natur. Mem.	Memoirs of the New Russian Society of Naturalists
N. S. Wales, Acclim. Soc. Report	Annual Reports (3, 6, and 7) of the Acclimatisation Society of N. S. W.
N. S. Wales Dept. Mines Report	Annual Report of the Department of Mines (and Agriculture), New South Wales
N. S. Wales, Entom. Soc. Trans.	The Transactions of the Entomological Society of New South Wales
N. S. Wales Linn. Soc. (Macleay Mem. Vol.)	Linnean Society of New South Wales. The Macleay Memorial Volume
N. S. Wales, Linn. Soc. Proc.	The Proceedings of the Linnean Society of New South Wales
N. S. Wales P.	New South Wales Patent
N. S. Wales, Phil. Soc. Trans.	Transactions of the Philosophical Society of New South Wales
N. S. Wales, Roy. Soc. J.	Journal and Proceedings of the Royal Society of New South Wales
N. S. Wales, Roy. Soc. Trans.	Transactions of the Royal Society of New South Wales
N. Y. Acad. Ann.	Annals of the New York Academy of Sciences, late Lyceum of Natural History
N. Y. Acad. Mem.	New York Academy of Sciences. Memoirs
N. Y. Acad. Trans.	Transactions of the New York Academy of Sciences. Late Lyceum of Natural History



N. Y. Acad. Med. Bull.	Bulletin of the New York Academy of Medicine
N. Y. Acad. Med. Trans.	Transactions of the New York Academy of Medicine
N. Y. Agric. Soc. Trans.	Transactions of the New York State Agricultural Society
N. Y. Bot. Club Bull.	Bulletin of the Torrey Botanical Club
N. Y. Entom. Soc. J.	Journal of the New York Entomological Society
N. Y. Insects Report	Report on the Noxious, Beneficial and other Insects of the State of New York
N. Y. J. Med.	New York Journal of Medicine and the Collateral Sciences
N. Y. Linn Soc Trans.	Transactions of the Linnaean Society of New York
N. Y. Lit. Phil. Soc. Trans.	Transactions of the Literary and Philosophical Society of New York
N. Y. Lyceum Ann	Annals of the Lyceum of Natural History of New York
N. Y. Lyceum, Proc	Proceedings of the Lyceum of Natural History in the City of New York
N. Y. Med. J.	New York Medical Journal
N. Y. Med. Repos.	Medical Repository of New York
N. Y. Med. Soc. Trans	Transactions of the Medical Society of the State of New York
N. Y. Mus. Bull.	University of the State of New York Bulletin of the New York State Museum
N. Y. Mus. Mem.	Memoirs of the New York State Museum
N. Zeal Inst. Trans	Transactions and Proceedings of the New Zealand Institute
N. Zeal. Inst Min. Engin Trans.	Transactions of the New Zealand Institute of Mining Engineers
N. Zeal J. Sci	The New Zealand Journal of Science
N. Zeal. P.	New Zealand Patent
N. Zeal. Pap. & Rep	New Zealand Papers and Reports relating to Minerals and Mining
Nachr. konig Ges.	Nachrichten von der koniglichen Gesellschaft der Wissenschaften zu Gottingen (Mathematische-physikalische Klasse)
Nancy, Acad Stanislas Mem.	Academie de Stanislas. Memoires de la Société (Royale) des Sciences, etc, de Nancy
Nancy Soc. Sci. Bull.	Bulletin de la Société des Sciences de Nancy
Nancy Soc. Sci. Mem.	Memoires de la Société (Royale) des Sciences, Lettres, et Arts de Nancy
Nancy Soc. Sci. Trav	Precis analytique des Travaux de la Société (Royale) des Sciences, Arts, et Agriculture de Nancy
Nantes J. Med.	Journal de la Section de Medecine de la Société Academique du departement de la Loire Inferieure
Nantes, Ann. Soc. Acad.	Annales de la Société Academique de Nantes et du departement de la Loire Inferieure
Nantes Soc. Sci. Natur. Bull.	Bulletin de la Société des Sciences naturelles de l'Ouest de la France
Napoli Accad. Aspir. Ann.	Annali della Accademia degli aspiranti Naturalisti
Napoli Accad. Atti	Atti della Reale Accademia delle Scienze Fisiche e Matematiche
Napoli Accad. Pontan. Atti	Atti dell' Accademia Pontaniana
Napoli Accad. Sci. Atti	Atti della Reale Accademia della Scienze e Belle Lettere; Sezione della Società R. Borbonica
Napoli Accad. Sci. Mem.	Memorie della R. Accademia della Scienze
Napoli Giorn. Mat.	See Giornale di Matemat.
Napoli, Atti Ist. Incorr.	Atti del Real Istituto d'Incoraggiamento alle Scienze Naturali di Napoli

Napoli Lucifero	Il Lucifero
Napoli Mus.	Museo di Letteratura e Filosofia
Napoli, Ann. Mus. Zool.	Annuario del Museo Zoologico della R. Università di Napoli
Napoli Rend.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche. (Sezione della Società Reale di Napoli)
Napoli Soc. Natur. Boll.	Bollettino della Società di Naturalisti in Napoli
Natl. Assoc. Retail Drug, Notes	The Journal of the National Association of Retail Druggists, Chicago
Natl. Disp.	National Dispensatory
Natl. Drug.	National Druggist
Natl. Ecl. Med. Assoc. Quart.	The National Eclectic Medical Association Quarterly, Cincinnati
Natl. Glass Budget	National Glass Budget
Natl. Inst. Bull.	Bulletin of the Proceedings of the National Institution for the Promotion of Science
Natur. Can.	Le Naturaliste Canadien. Bulletin de Recherches, Observations et Découvertes se rapportant à l'Histoire naturelle du Canada
Natur. Sicil.	Il Naturalista Siciliano. Giornale di Scienze Naturali
Natur. J.	The Naturalists' Journal
Naturaleza	La Naturaleza. Periodico científico de la Sociedad Mexicana de Historia Natural
Naturalist (Yorks)	The Naturalist: Journal of the West Riding Consolidated Naturalists' Society
Naturaliste	Le Naturaliste
Nature	Nature
Naturf.	Der Naturforscher
Natur. Hist. Review	The Natural History Review and Quarterly Journal of Science
Naturhist. Notizen	Naturhistorische und chemisch-technische Notizen nach den neuesten Erfahrungen
Naturhist. Tidsskr.	Naturhistorisk Tidsskrift
Naturwiss. Umschau	Naturwissenschaftliche Umschau der Chemiker-Zeitung
Chem. Ztg.	
Natuurk Tijdschr.	Natuurkundige Tijdschrift, inhoudende Phijsica, Chemie, Pharmacie, Nat. Hist. &c., uitg. van wege het Genootschap: "Tot nut en vergenoegen," te Arnhem.
Nauche, J. Galvan.	Journal du Galvanisme, de Vaccine, etc.
Naval Archit. Trans.	Transactions of the Institution of Naval Architects
Naval Sci.	Naval Science: a Quarterly Magazine for promoting the improvement of Naval Architecture, Marine Engineering, Steam Navigation, and Seamanship
Neapel Zool. Sta., Fauna & Flora	Fauna und Flora des Golfes von Neapel und der angrenzenden Meeres-Abschnitte herausgegeben von der Zoologischen Station zu Neapel
Neapel Zool. Sta. Mitth.	Mittheilungen aus der Zoologischen Station zu Neapel
Nebraska Univ. Stud.	University Studies. Published by the University of Nebraska
Nederl. Archiv.	See Selenka
Nederl. Archief Natuurk.	Nederlandsch Archief voor Genees-en Natuurkunde
Nederl. Bot. Ver. Versl. en Meded.	See Nederl. Kruidk. Arch.
Nederl. Dierk. Ver. Tijdschr.	Tijdschrift der Nederlandsche Dierkundige Vereeniging
Nederl. Entom. Ver.	See Tijdschr. Ent.

Nederl. Kruidk. Archief.	Nederlandsch Kruidkundig Archief
Nederl. Lancet	Nederlandsch Lancet. Tijdschrift aan de praktische Chirurgie, etc
Nederl. Tijdschr. Dierkunde	Nederlandsch Tijdschrift voor de Dierkunde, uitgegeven door het koninklijk Zoologisch Genootschap Natura Artis Magistra te Amsterdam
Nederl. Tijdschr. Geneesk.	Nederlandsch Tijdschrift voor Geneeskunde, tevens orgaan der Nederlandsche Maatschappij tot de Bevordering der Geneeskunst
Neuchatel Soc. Sci. Bull.	Bulletin de la Société des Sciences Naturelles de Neuchatel
Neues Bergmann J.	Neues bergmannisches Journal
Neues Jahr. Min.	Neues Jahrbuch für Mineralogie Geologie und Palaeontologie
Neues Lausitz. Mag.	Neues Lausitzisches Magazin; unter Mitwirkung der Oberlausitzischen Gesellschaft der Wissenschaften
Neue med.-chir. Ztg.	Neue medicinisch-chirurgische Zeitung
Neues Nord. Archiv.	Neues nordisches Archiv für Natur und Arzneykunde, verfasst von einer Gesellschaft nordischer Gelehrten
Neue Preuss. Provinz. Blatt.	Neue Preussische Provinzial-Blätter
Neu-Vorpommern Mitth.	Mittheilungen aus dem naturwissenschaftlichen Vereins für Neu-Vorpommern und Rugen in Greifswald
Newbury Field Club Trans.	Transactions of the Newbury District Field Club
Newcastle Chem. Soc. Trans.	Newcastle-upon-Tyne Chemical Society. Transactions
Newf. P.	Newfoundland Patent
Newman. Entom.	The Entomologist
Newport Natur. Hist. Soc. Proc.	Proceedings of the Newport Natural History Society
Nicholson J.	Journal of Natural Philosophy, Chemistry, and the Arts
Nick.	The Nickelodeon
Niederl. Archiv. Zool.	Niederländisches Archiv. für Zoologie
Niederöstrerr. Gewerb-Verh.	Verhandlungen des Niederösterreichischen Gewerbe-Vereins
Niederrhein. Ges. Naturk. Sitzber.	Sitzungsberichte der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn
Niederrhein. Ges. Organ.	Organ für die gesammte Heilkunde; herausgegeben von der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn
Nieuw Archief Wisk.	Nieuw Archief voor Wiskunde
Nîmes Soc. Sci. Bull.	Bulletin de la Société d'Etude des Sciences Naturelles de Nîmes
Nor. Amer. Med. Chir. Rev.	The North-American Médico-Chirurgical Review
Nor. Eng. Inst. Min. Engin. Trans	North of England Institute of Mining and Mechanical Engineers Transactions
Nor. Staff. Field Club Rep.	(The) North Staffordshire (Naturalists') Field Club (and Archaeological Society). Annual Report (and Transactions)
Nord. Brabant, Handel. prov. Genoots.	Handelingen van het provinciaal Genootschap van Kunsten en Wetenschappen in Nord Brabant
Nord France Soc. Linn. Bull.	Bulletin de la Société Linneenne du Nord de la France
Nord France Soc. Linn. Mem.	Memoires de la Société Linneenne du Nord de la France

Nord, Mem. Soc. Agric.	See Douai
Nord, Soc. Agric. Seance Publ.	Seance Publique de la Société d'Agriculture, Sciences, et Arts, etc., du département du Nord
Nordamerik. Monatsber.	Nordamerikanischer Monatsbericht für Natur- und Heilkunde
Norddeut. Landwirth	Der norddeutsche Landwirth
Nordisches Archiv.	Nordisches (u. Neues Nordisches) Archiv. für Naturkunde und Arzneiwissenschaft
Norf. Norw. Natur. Soc. Trans.	Transactions of the Norfolk and Norwich Naturalists' Society
Normandie	See Caen
Normandie Soc. Linn. Bull.	Bulletin de la Société Linneenne de Normandie
Normandie Soc. Linn. Mem.	Memoires de la Société Linneenne de Normandie
Normandie Soc. Linn. Seance Publ.	Seance Publiques de la Société Linneenne de Normandie
Norsk Tidsk. Vid. Litt.	Norsk Tidsskrift for Videnskab og Litteratur.
Norske Videnskab. Skrift.	Det Kongelige Norske Videnskabselskabs Skrifter i det 19 de Aarhundrede
Northampton Natur. Hist. Soc. J.	Journal of the Northampton(shire) Natural History Society and Field Club
Northern J. Med	Northern Journal of Medicine
Northumb. Natur. Hist Soc. Trans	Transactions of the Natural History Society of Northumberland, Durham, and Newcastle-upon-Tyne
Northwestern Drug.	Northwestern Druggist (The), Minneapolis
Norw. P.	Norwegian Patent
Notarisia	Notarisia Commentarium Phycologicum. La Notarisia. Commentario Ficológico Generale. Parte speciale della Rivista Neptunia
Notices of Judgment, U S. Dept. Agric	Notices of Judgment, U. S. Department of Agriculture
Notiz. Archit. Ver. Niederrhein	Notizblatt des Architekten und Ingenieur Vereins für Niederrhein und Westfalen
Notiz Riga	Notizblatt des technischen Vereins zu Riga
Nouv. Ann Math	Nouvelles Annales de Mathematiques
Nouv. Archiv. Miss Sci.	Nouvelles Archives des Missions Scientifiques et Littéraires
Nouv. remedes	Nouveaux remedes, Paris
Nova Acta Acad. Nat. Curios	Novorum Actorum Academiae Caesareae Leopoldino-Carolinae Germanicae Naturae Curiosorum
Nova Scotia Inst. Sci. Proc. & Trans	(The) Proceedings and Transactions of the Nova Scotian Institute of (Natural) Science
Nova Scotia, Trans. Lit. Sci. Soc	Transactions of the Literary and Scientific Society of Nova Scotia
Novitates Zool.	Novitates Zoologicae. A Journal of Zoology in connection with the Tring Museum
Nuov. Ann Sci Natur.	Nuovi Annali delle Scienze naturali
Nuov. Antol. Sci.	Nuova Antologia di Scienze, Lettere (Lettere, Scienze) ed Arti
Nuov. Cimento	Il Nuovo Cimento, Giornale di Fisica, di Chimica, e di Storia Naturale
Nuov. Giorn. Bot. Ital.	Nuovo Giornale Botanico Italiano (e Bullettino della Società Botanica Italiana)
Nuov. Notarisia	La Nuova Notarisia. Rassegna (trimestrale) consacrata allo Studio delle Alghe (e Corollario alla "Sylloge Algarum Omnium")
Nürnb. Natur. Ges. Abh.	Abhandlungen der Naturhistorischen Gesellschaft zu Nürnberg
Nye Hygaea	Nye Hygaea

Nyt Mag. Naturvid.	Nyt Magazin for Naturvidenskaberne
Nyt Tidsskr. Fys. Kem.	Nyt Tidsskrift for Fysik og Kemi.
Oberhess. Ges. Ber.	Berichte der Oberhessischen Gesellschaft für Naturkunde und Heilkunde in Giessen
Odontol. Soc. Trans.	Transactions of the Odontological Society of Great Britain
Oesterr. Bot. Zts	Oesterreichische Botanische Zeitschrift
Oesterr. Chem. Ztg.	Oesterreichische Chemiker Zeitung
Oesterr. landw. Wochenbl.	Oesterreichisches landwirtschaftliches Wochenblatt
Oesterr. Med. Jahr.	Medicinisches Jahrbuch des k. k. Oesterreichischen Staates
Oesterr. Med. Wochenschr.	Oesterreichische Medicinische Wochenschrift, als Ergänzungsblatt der medicinischen Jahrbücher
Oesterr. Wochenschr.	Oesterreichische Wochenschrift für Wissenschaft, Kunst, und öffentliches Leben
Oesterr. Zts. Berg. Huttenw.	Oesterreichische Zeitschrift für Berg- und Huttenwesen
Oesterr.-ung. Zts. Zuckerind.	Oesterreichisch-ungarische Zeitschrift für Zuckerindustrie und Landwirtschaft
Off. Gaz.	Official Gazette, United States Patent Office
Offenbach. Ver. Naturk. Ber.	Beicht des Offenbacher Vereins für Naturkunde über seine Thatigkeit
Oil Colour J.	Oil and Colourman's Trade Journal
Oil, Paint Drug Rep	Oil, Paint and Drug Reporter
Oise	See Beauvais
Oise Mem. Soc. Acad.	Memoires de la Société Academique d'Archeologie, Sciences, et Arts du departement de l'Oise
Oken Isis	Isis, oder Encyclopadische Zeitung
Omaha Drug	Omaha Druggist (The), Omaha
Omodei Ann. Univ.	Annali Universali di Medicina
Ontario Entom. Soc. Rep	Report of the Entomological Society of Ontario
Oporto	See Porto
Ophthalm. Bibliothek	Ophthalmologische Bibliothek
Ophthalm. Hosp. Reports	Ophthalmic Hospital Reports and Journal of the Royal London Ophthalmic Hospital
Ophthalmic Rev.	The Ophthalmic Review a Quarterly Journal of Ophthalmic Surgery and Science
Organ Rubenzuckerind	Organ des Centralvereins für Rubenzuckerindustrie
Orgelb	Die Orgelbauzeitung
Orleans Ann.	Annales de la Société Royale des Sciences, Belles-Lettres, et Arts d'Orleans
Orleans, Bull	Bulletin des Sciences Physiques, Medicales, et d'Agriculture d'Orleans
Ornis	Ornis, oder das Neuste und Wichtigste der Vogelkunde, etc.
Ornith. Jahr.	Ornithologisches Jahrbuch
Ornith. Monatsber.	Ornithologische Monatsberichte
Ornithol.	The Ornithologist
Ornithol. Ool.	The Ornithologist and Oologist
Örsted Tidsskrift	Tidsskrift for Naturvidenskaberne
Orvos-Termesz. Ertes.	Orvos-Termeszettudományi Ertesito a Kolozsvári Orvos-Termeszettudományi Tarsulat és az Erdélyi Museum-Egyet. Termeszettudományi Szakosztálynak az. szakuleseiről. (Medical and Natural History Proceedings of the sections of the Klausenburg Medical and Natural History Society and of the Natural History section of the Museum Association of Transylvania)

Osnabruck, Jahr.	Jahresbericht des Naturwissenschaftlichen Vereins zu Osnabruck
Ottawa Field-Natur Club	Ottawa Field-Naturalists' Club Transactions
Trans	
Ottawa Natur.	The Ottawa Naturalist
Ouest France Soc. Sci. Nat.	See Nantes . .
Bull	
Oversigt K. D a n s k e	Oversigt over det Kongelige Danske Videnskabernes
Vidensk. Selsk Forh.	Selskabs Forhandlinger
Pacific Drug Rev.	Pacific Drug Review, Portland
Pacific Pharm.	Pacific Pharmacist
Padova, Mem. Acad	Memorie dell' Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Nuovi Saggi	Nuovi Saggi dell' Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Rivista Period	Rivista Periodica dei Lavori della I. R. Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Soc. Sci. Atti	Atti della Societa Veneto-Trentina di Scienze naturali
Padova Soc. Sci. Bull.	Bullettino della Societa Veneto-Trentina di Scienze Naturali residente in Padova
Palermo Accad. Atti	Atti della Reale Accademia di Scienze, Lettere e Belle Arti di Palermo
Palermo Circ. Mat. Rend.	Rendiconti del Circolo Matematico di Palermo
Palermo, Effemeridi	Effemeridi scientifiche e letterarie per la Sicilia; coi Lavori del R. Istituto d'Incoraggiamento per la Sicilia
Palermo, Giorn Sci Natur.	Giornale di Scienze naturali ed economiche, pubblicato per Cura della Societa di Scienze naturali ed economiche di Palermo
Palermo, Mem. Spettrosc Ital	Memorie della Societa degli Spettroscopisti Italiani
Palermo Oss. Bull Meteorol	Bullettino Meteorologico del Reale Osservatorio di Palermo
Palermo Oss Ossvz. Meteorol.	R. Osservatorio di Palermo. Stazioni di Valverde Osservazioni meteorologiche
Palomba, Raccolta	Raccolta di Lettere, etc, intonno alla Fisica ed alle Mathematiche
Palyamunkak	Palyamunkak Termerzetlud (Prize Essays of the Hungarian Academy)
Pander, Beitr. Naturk.	Beitrage zur Naturkunde aus den Ostseeprovinzen Russlands
Paper	Paper
Paper-Maker Brit. Trade J.	Paper Maker and British Trade Journal
Paper Makers' Monthly J.	Paper Makers' Monthly Journal
Paper Making	Paper Making
Paper Mill	Paper Mill and Woodpulp News
Papers Naval Archit.	Papers on Naval Architecture and other subjects connected with naval science
Paper Trade J.	Paper Trade Journal
Papier-Fabr.	Papier-Fabrikant, Der
Papier Ztg.	Papier Zeitung
Papierhandel	Der Papierhandel
Papilio	Papilio
Papir J.	Papir Journalen
Par. P.	Paraguay Patent
Para, Mus Hist. Natur. Bol.	Boletim do Museu Paraense de Historia Natural e Ethnographia
Paris, Acad. Med. Bull.	Bulletin de l'Academie de Medecine

Paris, Acad. Med. Mem.	Memoires de l'Academie de Medecine
Paris, Acad. Sci. Compt. rend.	Comptes Rendus hebdomadaires des Seances de l'Academie des Sciences
Paris, Acad. Sci. Mem.	Memoires de l'Academie des Sciences de l'Institut de France
Paris, Ann. Cerc. Med.	Annales du Cercle Medecale
Paris, Ann. Conserv.	Annales du Conservatoire des Arts et Metiers
Paris, Ann. Ecole Norm.	Annales scientifiques de l'Ecole Normale Supérieure
Paris, Ann. Ponts Chauss.	Annales des Ponts et Chaussées. Memoires et documents relatifs a l'Art des Constructions et au Service de l'Ingénieur
Paris, Ann. Soc. Entom.	Annales de la Société Entomologique de France
Paris, Annaes Sci.	Annaes das Sciencias, etc., por huma Sociedade de Portuguezes residentes em Paris
Paris, Annu. Med. Chir. Hosp.	Annuaire medico chirurgical des Hopitaux, etc., de Paris
Paris, Annu. Soc. Met.	Annuaire de la Société Meteorologique de France
Paris, Anthropol. Soc. Bull.	Bulletin de la Société d'Anthropologie de Paris
Paris, Anthropol. Soc. Mem.	Memoires de la Société d'Anthropologie de Paris
Paris, Bull. Fac. Med.	Bulletins de la Faculté de Medecine de Paris et de la Société établie dans son sein
Paris, Bull. Soc. Aerost.	Bulletin de la Société Aerostatique et Meteorologique de France
Paris, Bull. Soc. Sci. Natur.	Bulletin de la Société des Sciences Naturelles de France
Paris, Bur. Long. Annu.	Annuaire pour l'An.. publie par le Bureau des Longitudes
Paris, Caus. Sci.	Causeries Scientifiques de la Société Zoologique de France
Paris, Club Alpin Franc. Annu.	Annuaire du Club Alpin Français
Paris, Com. Intl. Carte Ciel. Bull.	Institut de France. Academie des Sciences. Bulletin du Comité International Permanent pour l'Execution Photographique de la Carte du Ciel
Paris Congr. Bot. Act.	Actes du Congrès International de Botanique tenu a Paris in aout 1867
Paris Congr. Bot. Compt. rend.	. Comptes Rendus. Congrès International de Botanique et d'Horticulture
Paris, Congr. Med. Intl.	Congrès Medical International de Paris, 1867
Paris, Ecole Norm. Ann.	Annales Scientifiques de l'Ecole Normale Supérieure, publies sous les auspices du Ministre de l'Instruction Publique
Paris, Ecole Poly. Corresp.	Correspondance sur l'Ecole Polytechnique, a l'usage des Elèves de cette École
Paris, Ecole Poly. J.	Journal de l'Ecole Polytechnique publie par le Conseil d'Instruction de cet Etablissement
Paris, Ethnog. Soc. Compt. rend.	Comptes Rendus des Seances de la Société d'Ethnographie Americaine et Orientale
Paris, Hautes Etudes Bibl.	Bibliothèque de l'Ecole des Hautes Etudes. Section des Sciences Naturelles
Paris, Ingen. Civ. Mem.	Memoires et Compte Rendu des Travaux de la Société des Ingenieurs Civils (de France)
Paris, J. Bot.	Journal de Botanique, par une Société de Botanistes
Paris, J. Chir.	Journal de Chirurgie
Paris, Lab. Histol. Trav.	Ecole Pratique des Hautes Etudes. Laboratoire d'Histologie du College de France. Travaux
Paris, Mem. Acad. Med.	Memoires de l'Academie (Royale) de Medecine
Paris, Mem. Acad. Sci.	Memoires de l'Academie des Sciences
Paris, Mem. Inst.	Memoires de la Classe des Sciences mathematiques et physiques de l'Institut

Paris, Mem. Soc. Savants	Memoires des Sociétés Savants et Litteraires de la Republique Francaise
Paris, Mem. Savants Etrang.	Memoires presentes par divers Savants a l'Academie des Sciences de l'Institut de France
Paris, Mem. Soc. Ethnol.	Memoires de la Société Ethnologique
Paris, Mem. Soc. Fac. Med.	Memoires de la Société de la Faculte de Medecine
Paris, Mem. Soc. Linn.	Memoires de la Société Linneenne de Paris
Paris, Mem. Soc. Med.	Memoires de la Société de Medecine
Paris, Mem. Soc. Med. Observ.	Memoires de la Société Medicale d'Observation
Paris, Mus. Hist. Natur. Ann.	Annales du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Archiv.	Archives du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Bull.	Bulletin du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Cent.	Centenaire de la Fondation du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Mem.	Memoires du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Nouv. Ann.	Nouvelles Annales du Museum d'Histoire Naturelle
Paris, Mus. Hist. Natur. Nouv. Archiv.	Nouvelles Archives du Museum d'Histoire Naturelle
Paris Obs. Ann.	Annales de l'Observatoire de Paris
Paris, Obs. Montsouris Annu.	(Ville de Paris) Annuaire de l'Observatoire (municipal de Paris, dit Observatoire) de Montsouris.
Paris, Poids Mes. Proc. Verb.	Comite International des Poids et Mesures. Procès-Verbaux des Seances
Paris, Poids Mes. Trav. Mem.	Travaux et Memoires du Bureau International des Poids et Mesures
Paris, Recueil Soc. Med. Observ.	Recueil des travaux de la Société Medicale d'Observation de Paris
Paris, Recueil. Trav. Soc. Med. Allemande	Recueil des Travaux lus a la Société Medicale Allemande de Paris
Paris, Soc. Acclim. Bull.	Bulletin de la Société Zoologique d'Acclimatation
Paris, Soc. Anat. Bull.	Bulletin de la Société Anatomique de Paris
Paris, Soc. Anthropol. Bull.	Bulletins de la Société d'Anthropologie de Paris
Paris, Soc. Anthropol. Mem.	Memoires de la Société d'Anthropologie de Paris
Paris, Soc. Biol. Mem.	Comptes Rendus des Seances et Memoires de la Société de Biologie
Paris, Soc. Chir. Bull.	Bulletin de la Société de Chirurgie de Paris
Paris, Soc. Chir. Mem.	Memoires de la Société de Chirurgie de Paris
Paris, Soc. Entom. Ann.	Annales de la Société Entomologique de France
Paris, Soc. Entom. Bull.	Bulletin de la Société Entomologique de France
Paris, Soc. Geogr. Bull.	Bulletin de la Société de Geographie
Paris, Soc. Geogr. Compt. rend.	Compte Rendu des Seances de la Société de Geographie et de la Commission Centrale
Paris, Soc. Hist. Natur. Mem.	Memoires de la Société d'Histoire Naturelle de Paris
Paris, Soc. Ing. Civ. Mem.	Memoires et Comptes Rendus des Travaux de la Société des Ingenieurs Civils
Paris Soc. Linn. Bull.	Bulletin mensuel de la Société Linneenne de Paris
Paris, Soc. Math. Bull.	Bulletin de la Société Mathematique de France
Paris, Soc. Med. Emul. Bull.	Bulletins de la Société Medicale d'Émulation
Paris, Soc. Med. Emul. Mem.	Memoires de la Société Medicale d'Émulation
Paris, Soc. Philom. Bull.	Bulletin des Sciences de la Société Philomathique de Paris



Paris, Soc. Philom Mem Cent.	Memoires publies par la Société Philomathique a l'occasion du Centenaire de sa Fondation, 1788-1888
Paris, Soc. Philom Nouv Bull.	Nouveau Bulletin des Sciences de la Société Philomatique de Paris
Paris, Soc. Philom Proc Verb.	Extraits des Procès-Verbaux des Seances de la Société Philomathique
Paris, Soc Phys Seances	Seances de la Société Française de Physique
Paris, Soc Speleol Mem	Memoires de la Société de Speleologie
Paris Tow Nauk Scisl Pam.	Pamiętnik Towarzystwa Nauk Scislych w Paryżu
Paris, Trav Soc. Amat	Notice des Travaux de la Société des Amateurs des Sciences physiques et naturelles de Paris
Parlatore, Giorn Bot	Giornale Botanico Italiano
Parma, Giorn Soc Med Chir	Giornale della Società Medico-Chirurgica di Parma
Passau Ber Nat. Ver	.. Bericht des Naturhistorischen Vereins in Passau fur...
Passau, Jahr Naturhist Ver	Jahresbericht des Naturhistorischen Vereins
Pathol Soc Trans	Transactions of the Pathological Society of London
Pavia Ist. Bot. Atti	Atti dell' Istituto Botanico dell' Università di Pavia, Seguito dell' Archivio Triennale del Laboratorio di Botanica Crittogamica
Pavia Lab. Crittog Archiv	Archivio del Laboratorio di Botanica Crittogamica presso la R Università di Pavia
Peabody Acad Mem.	Memoirs of the Peabody Academy of Science
Peabody Acad. Report	Sixth Annual Report of the Trustees of the Peabody Academy of Science
Penn Univ. Publ.	Publications of the University of Pennsylvania
Penzance Soc Trans	Transactions of the Natural History and Antiquarian Society of Penzance
Perf Essent Oil Rec	Perfumery and Essential Oil Record
Perthsh Soc Sci Trans & Proc.	Transactions and Proceedings of the Perthshire Society of Natural Science
Peru P	Peruvian Patent
Pet. Nouv. Entom	Petites Nouvelles Entomologiques
Petermann, Mitth	Dr. A. Petermann's Mittheilungen aus Justus Perthes' Geographischer Anstalt
Peters, Zts	Zeitschrift fur populare Mittheilungen aus dem Gebiete der Medicin, Chirurgie, und Pharmacie, in Verbindung mit einem Vereine von Aerzten und Pharmaceuten der Herzogthumer Schleswig und Holstein
Petroleum	Petroleum
Petroleum Gaz.	Petroleum Gazette
Petroleum Rev.	Petroleum Review
Pfluger, Archiv. Physiol	Archiv fur die gesammte Physiologie des Menschen und der Thiere
Pharm.	Pharmakologie
Pharm -Ber Deut.-Arzbuch.	Pharmakopoe-Bericht. Die vegetabilischen Drogen des Deutschen Arzneibuches, 5te. Ausgabe, Caesar & Loretz, Halle
Pharm. Centr.	Pharmaceutisches Central-Blatt
Pharm. Centralh	Pharmaceutische Centralhalle fur Deutschland
Pharm. Era	Pharmaceutical Era
Pharm. J.	The Pharmaceutical Journal (and Transactions)
Pharm. Post	Pharmazeutische Post
Pharm. Weekblad	Pharmazeutische Weekblad
Pharm. Ztg.	Pharmazeutische Zeitung

Pharm. Zts.	Pharmazeutische Zeitschrift
Pharm. Zts. Russland	Pharmaceutische Zeitschrift für Russland
Phil. Mag.	Philosophical Magazine
Phil. Stud.	Philosophische Studien
Phil. Trans.	Philosophical Transactions of the Royal Society of London
Phila. Acad. Natur. Sci. J.	Journal of the Academy of Natural Sciences of Philadelphia
Phila. Acad. Natur. Sci. Proc.	Proceedings of the Academy of Natural Sciences of Philadelphia
Phila. Amer. Entom. Soc.	See Amer. Entom. Soc.
Phila. Coll. Pharm. Journ.	Journal of the Philadelphia College of Pharmacy
Phila. Eng. Club	Proceedings of the Engineers' Club of Philadelphia
Phila. Entom. News	Entomological News (and Proceedings of the Entomological Section of the Academy of Natural Sciences of Philadelphia)
Phila. Entom. Soc. Proc.	Proceedings of the Entomological Society of Philadelphia
Phila. Med. Mus.	Philadelphia Medical Museum
Phila. Med. Phys. J.	The Philadelphia Medical and Physical Journal
Phila. Phot.	The Philadelphia Photographer
Philippine J. Sci.	Philippine Journal of Science
Phot. Archiv	Photographisches Archiv
Phot. Bull.	Anthony's Photographic Bulletin
Phot. Chronik.	Photographische Chronik und allgemeine Photographen-Zeitung
Phot. J.	Wilhelm Horn's Photographische Journal
Phot. Corr. (Korr.)	Photographische Korrespondenz
Phot. Mag.	Photographisches Magazine
Phot. Mitth.	Photographische Mittheilungen
Phot. Monats.	Photographische Monatshefte
Phot. News	Photographic News
Phot. Rundsch.	Photographische Rundschau und Photographisches Centralblatt
Phot. Soc. J.	Journal of the Photographic Society of London
Phot. Soc. Trans.	Trans. of the Photographic Society of London
Phot. Times	The Photographic Times
Phot. Wochenbl.	Photographisches Wochenblatt
Phot. World	The Photographic World
Phot. Centr.	Photographisches Centralblatt
Phot. Ztg.	Deutsche Photographen-Zeitung
Phys. Rev.	Physical Review
Physikal.-Chem. Zentr.	Physikalisch-chemisches Zentralblatt
Physikal. Meddel.	Physikalske Meddelelser
Physikal. Zts.	Physikalische Zeitschrift
Physiol. Russe	Le Physiologiste Russe
Physiol. Soc. Proc.	See J. Physiol.
Phytologist	The Phytologist: a popular Botanical Miscellany
Pisa, Ann. Scuola Norm.	Annali della R. Scuola Normale Superiore di Pisa. Scienze Fisiche e Matematiche
Pisa, Ann. Univ. Tosc. Sci. Cosm.	Annali della Università Toscana. Scienze Cosmologiche
Pisa, Miscell. Med. Chir.	Miscellanea medico-chirurgico-farmaceutiche raccolte in Pisa
Pisa, Nuov. Giorn.	Nuovo Giornale de' Letterati
Pisa Soc. Sci. Proc.	Atti della Società Toscana di Scienze Naturali residente in Pisa

Pisa Soc. Tosc. Atti (Mem.)	Atti della Societa Toscana di Scienze Naturali residente in Pisa. Memorie
Pisa Soc. Tosc. Atti (Proc. Verb.)	Atti della Societa Toscana di Scienze Naturali residente in Pisa. Processi Verball
Pistoja, Atti Accad.	Atti della R. Accademia Pistojese di Scienze, Lettere, ed Arti, Memorie di Matematica e Fisca
Plant World	Plant World, The
Plata Mus. Anales	Anales del Museo de La Plata. Materiales para la Historia fisica y moral del Continente Sud-Americano
Plata Mus. Revista	Revista del Museo de La Plata
Plon Biol. Sta. Forschungsber	Forschungsberichte aus der Biologischen Station zu Plon
Plymouth Inst. Trans.	Annual Reports and Transactions of the Plymouth Institution and Devon and Cornwall Natural History Society
Pogg. Ann.	Poggendorff's Annalen der Physik und Chemie
Pogg. Ann. Beibl.	Poggendorff's Annalen der Physik und Chemie Beiblatter
Poligrafo	Il Poligrafo. Giornale di Science, Lettere, ed Arti
Polit.	Il Politecnico
Pollichia, Jahr.	Jahresbericht der Pollichia, eines naturwissenschaftlichen Vereins der Baierischen Pfalz (der Rheinpfalz)
Polsk. Tow. Przyrod. Koper- nika	See Kosmos (Lwow)
Poly. Centr.	Polytechnisches Centralblatt
Poly. Centralh.	Polytechnische Centralhalle
Poly. Mitth.	Polytechnische Mittheilungen
Poly. Notiz.	Polytechnisches Notizblatt
Polygraph. Centr.	Polygraphisches Centralblatt
Pommer, Zts.	Schweizerische Zeitschrift fur Natur- und Heilkunde
Pop. Mag. Anthropol.	The Popular Magazine of Anthropology
Pop. Sci. Mon.	Popular Science Monthly
Popular Sci. Rev.	The Popular Science Review, a Quarterly Miscellany of entertaining and instructive articles on Scientific subjects
Pontif. Univ. Gregor.	Pontificia Universita Gregoriana. Continuazione del Bullettino Meteorologico dell' Osservatorio del Collegio Romano
Port. P.	Portuguese Patent
Portland, Soc. Natur. Hist. Proc.	Proceedings of the Portland Society of Natural History
Porto, Ann. Soc. Lit.	Annacs da Sociedade Lit. Portuense
Porto Soc. Instruc. Rev.	Revista da Sociedade de Instrucao do Porto
Potsdam Astrophys. Obs. Publ.	Publicationen des Astrophysikalischen Observatoriums zu Potsdam
Pottery Gaz.	Pottery Gazette
Pottery and Glass	Pottery and Glass
Power	Power
Prace Mat.-Fiz.	Prace Matematyczno-Fizyczne. (Mathematical and Physical Papers)
Pract. Drug.	Practical Druggist and Pharmaceutical Review of Reviews, New York
Pract. Mag.	The Practical Magazine (London)
Pract. Mechan. J.	The Practical Mechanics Journal
Practitioner	The Practitioner
Prag, Abh.	Pojednani Kral. Ceske Spolecnosti Nauk. Abhandlungen der Königl. Böhmischen Gesellschaft der Wissenschaften

Prag, Ceske Ak. Fr. Jos. Pam.	Pomátník na oslavu padesáttkeho panovníckeho jubilea jeho Velicenstva Cisare a Krale Frantiska Josefa I. Vydala Ceska Akademie Cisare Frantiska Josefa pro Vedy, Slovesnost a Umeni. (Memoirs in celebration of the fifty years Jubilee of the reign of H. I. & R. M. Francis Joseph I. Published by the Bohemian Imperial Francis Joseph Academy of Science, Literature and Art)
Prag, Ceske Akad. Fr. Jos. Rozpr. (Trida 2)	Rozpravy Ceske Akademie Cisare Frantiska Josefa pro Vedy, Slovesnost a Umeni v Praze (Trida II.) (Transactions of the Bohemian Imperial Francis Joseph Academy of Science, Literature and Art in Prague. Class II)
Prag, Fr. Jos. Acad. Sci. Bull.	Academie des Sciences de l'Empereur Francois Joseph I. Bulletin International
Prag, Jahr. Bohm. Mus.	Jahrbucher des Bohmischen Museums fur Natur- und Landeskunde
Prag, Jahr. Realschule	Jahresbericht der k. k. Bohmischen Ober-Realschule zu Prag
Prag, Lotos Abh.	Abhandlungen des Deutschen Naturwissenschaftlich-Medicinischen Vereines fur Bohmen "Lotos"
Prag, Monatschr. Mus.	Monatsschrift der Gesellschaft des vaterlandischen Museums in Bohmen
Prag, Sitzber.	Zpravy o Zasedani (Vestník) Kralovské Ceske Společnosti Nauk. Trida Mathematicko-Prirodovědecká. Sitzungsberichte der Königl. Bohmischen Gesellschaft der Wissenschaften. Mathematisch-Naturwissenschaftliche Classe
Prag, Sternw. Magn. Meteorol. Beob.	Magnetische und Meteorologische Beobachtungen an der K. K. Sternwarte zu Prag
Prag, Verh.	Verhandlungen der Gesellschaft des vaterlandischen Museums in Bohmen
Prag, Vierteljahrsschr.	Vierteljahrsschrift für die praktische Heilkunde
Pressburg, Corresp. Blatt.	Correspondenzblatt des Vereins für Naturkunde zu Pressburg
Pressburg, Verh.	Verhandlungen des Vereins für Naturkunde zu Pressburg
Presse Sci.	Presse Scientifique des Deux Mondes
Preuss. Bot. Ver. Sitzber.	See Königsberg Schriften
Preuss. Geod. Inst. Publ.	Publication des Königl. Preuss. Geodatischen Instituts
Preuss. Geod. Inst. Veröff.	Veröffentlichung des Königl. Preussischen Geodatischen Instituts
Preuss. Landes-Oekon.-Kolleg. Archiv.	See Landw. Jbuch
Pribram Bergakad.	See Wien, Berg- u. Huttenm. Jbuch
Princeton Mus. Contr.	Contributions from the (E. M.) Museum of Geology and Archaeology of Princeton College
Pringsheim, Jahr. Wiss. Bot. Print. Reg.	Jahrbucher für Wissenschaftliche Botanik Printers' Register
Prog. agric. viti.	Progres agricole et viticole
Proc. Amer. Acad.	Proceedings of the American Academy of Arts Sciences
Proc. Amer. Inst. Elec. Eng.	Proceedings of the American Institute of Electrical Engineers
Proc. Amer. Micro. Soc.	Proceedings of the American Microscopical Society
Proc. Amer. Pharm. Assoc.	Proceedings of the American Pharmaceutical Association
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society

Proc. Amer. Soc. Civil Eng	Proceedings of the American Society of Civil Engineers
Proc. Amer. Soc. Micro	Proceedings of the American Society of Microscopists
Proc Amer. Soc. Test. Mat.	Proceedings of the American Society for Testing Materials
Proc Amer. Water Works Assoc.	Proceedings of American Water Works Association
Proc. Assoc. Off. Agric. Chem.	Proceedings of the Association of Official Agricultural Chemists, Washington
Proc Austral Inst. Min Eng	Proceedings Australian Institute of Mining Engineers
Proc. Cambr. Phil Soc	Proceedings of the Cambridge Philosophical Society
Proc. Chem Soc.	Proceedings of the Chemical Society (London)
Proc. Eng Soc Western Penn	Proceedings of the Engineers' Society of Western Pennsylvania
Proc Inst Civil Eng.	Proceedings of the Institution of Civil Engineers
Proc Inst Mech Eng	Proceedings of the Institution of Mechanical Engineers
Proc. Natl Wholesale Drug Assoc	Proceedings of the National Wholesale Druggists' Association
Proc Physiol. Soc	Proceedings of the Physiological Society
Proc. Roy Soc. Edinb	Proceedings of the Royal Society of Edinburgh
Proc. Roy. Soc London	Proceedings of the Royal Society of London
Proc Roy. Soc Med	Proceedings of the Royal Society of Medicine
Proc. Soc Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine
Proc U. S. Naval Inst	Proceedings of U. S Naval Institute
Progres Med.	Le Progres Medical. Journal de Medecine, de Chirurgie et de Pharmacie
Progressive Age	Progressive Age
Propogation ind	La Propogation industrielle. Revue mensuelle illustre des inventions, machines, appareils et procedes de la France, etc
Prov. Med Assoc. J.	Journal of the Provincial Medical Association
Prov. Med. Surg Assoc Trans.	Transactions of the Provincial Medical and Surgical Association
Psyche	Psyche. Organ of the Cambridge Entomological Club
Psychol Med J	Journal of Psychological Medicine
Publ Carnegie Inst	Publications of the Carnegie Institution of Washington
Publ ind	Publication industrielle des machines par Armengaud
Public Analysts Proc	Proceedings of the Society of Public Analysts
Public Health	Public Health
Pulp Paper Mag Can	Pulp and Paper Magazine of Canada
Pure Products	Pure Products. Scientific Station for Pure Products, New York
Puy, Soc Agric Ann	Annales de la Société d'Agriculture, Sciences, etc , du Puy
Quart J. Chem Soc.	Quarterly Journal of the Chemical Society
Quart. J. Dent Sci	Quarterly Journal of Dental Science
Quart. J exp. Physiol	Quarterly Journal of experimental Physiology
Quart. J. Geol. Soc	Quarterly Journal of the Geological Society
Quart. J. Math.	The Quarterly Journal of Pure and Applied Mathematics
Quart. J Micro. Sci.	Quarterly Journal of Microscopical Science
Quart. J. Micro. Soc.	Quarterly Journal of the Microscopical Society
Quart. J. Sci.	The Journal of Science and the Arts Continued as the Quarterly Journal of Science, Literature, and Arts

Quebec, Lit. Hist. Soc. Trans.	Transactions of the Literary and Historical Society of Quebec
Queensl. P.	Queensland Patent
Queensl. Annu. Rep. Brit. N. Guinea	Annual Report on British New Guinea
Queensl. Natur. Hist. Soc. Trans.	Transactions of the Natural History Society of Queens- land
Queensl. Mus. Ann	Annals of the Queensland Museum
Queensl. Roy. Soc. Proc.	The Proceedings of the Royal Society of Queensland
Quekett Micro. Club J.	Journal of the Quekett Microscopical Club
Quetelet, Corresp. Math.	Correspondance Mathematique et Physique
Radium	Radium, Le
Railroad Eng. J.	The Railroad and Engineering Journal. The Amer- ican Railroad Journal and Van Nostrand's Engi- neering Magazine have been consolidated in this publication
Ranuzzi, Annuario Geogr.	Annuario geografico Italiano
Rass. minerar.	Rassegna mineraria metallurgica e chimica
Rauch Staub	Rauch und Staub
Rayer, Archiv.	Archives de Medecine comparee
Reclam, Kosmos	Kosmos Zeitschrift fur angewandte Naturwissen- schaften
Records Min.	Records of Mining
Recueil Math. (Moscou)	Recueil Mathematique Publie par la Société Mathe- matique de Moscou
Rec. Trav. Chim. Pays- Bas	Recueil des Travaux Chimiques des Pays-Bas (et de la Belgique)
Rec. Zool. Suisse	Recueil Zoologique Suisse, comprenant l'Embryologie, l'Anatomie et l'Histologie comparees, la Physiologie, l'Ethologie, la Classification des Animaux vivants et fossiles
Regensburg Bot. Ges.	See Flora
Regensburg Bot. Ges. Denkschr.	Denkschriften der Königlich (Bayerischen) Botan- ischen Gesellschaft zu Regensburg
Regensburg, Bot. Ztg.	Botanische Zeitung, herausg. von der k. Baier. Botan- ischen Gesellschaft zu Regensburg
Regensburg, Korresp. Blatt.	Korrespondenz-Blatt des Zoologisch-mineralogischen Vereins in Regensburg
Reichert, Archiv.	Archiv fur Anatomie, Physiologie, und wissenschaft- liche Medicin
Reil, Archiv.	Archiv. fur die Physiologie
Reimann's Ztg.	Reimann's Farberzeitung
Reims, Seances Acad.	Seances et Travaux de l'Academie de Reims
Rend. soc. chim. ital.	Rendiconti della societa chimica italiana
Rep.	Repertorium, Repertoire Repertory
Rep. Anal. Chem.	Repertorium der analytischen Chemie ..Organ des Vereins Analytischer Chemiker
Rep. Anat. Physiol.	Repertoire generale d'Anatomie et de Physiologie pathologiques et de Clinique chirurgicale
Rep. Chim.	Repertoire generale de Chimie (1901- ), G. Jaubert
Rep. Chim. pure (appl.)	Repertoire de Chimie pure (et appliquée) (Societe Chimique de Paris, 1859-1864)
Rep. Pat. Inv.	The Repertory of Patent Inventions and other dis- coveries and improvements in arts, manufactures and agriculture
Rep. Math.	Repertorium der literarischen Arbeiten aus dem Gebiete der reinen und angewandten Mathematik

Rep. Meteorol.	Repertorium fur Meteorologie, herausgegeben von der Kaiserlichen Akademie der Wissenschaften
Rep. Pharm.	Repertorium fur die Pharmacie
Rep. Phys	Repertorium der Physik
Rep. Phys -Tech	See Carl
Rep. Chem. Lab. Amer. Med. Ass.	Reports of the Chemical Laboratory of the American Medical Association, Chicago
Rep. Council Pharm Chem	Reports of the Council of Pharmacy and Chemistry, American Medical Association, Chicago
Rep. H. M. Insp. Expl.	Report of His Majesty's Inspectors of Explosives
Rep. N. Y. Bd Pharm.	Report of the New York State Board of Pharmacy
Rev. Anthropol.	Revue d'Anthropologie
Rev. Artill	Revue d'Artillerie
Rev. Biol. Nord France	Revue Biologique du Nord de la France
Rev. Bot.	Rev. de Botanique. Bulletin mensuel de la Société Française de Botanique
Rev. Bryol.	Revue Bryologique Bulletin bimestriel consacre a l'Etude des Mousses et des Hepatiques
Rev. chim. ind.	Revue de chimie industrielle et La revue de physique et de chimie
Rev. Cours. Sci.	Revue des Cours Scientifiques de la France et de l'Etranger
Rev deux Mondes	Revue des deux Mondes (Paris)
Rev. Entom	Revue d'Entomologie publiee par la Société Française d'Entomologie
Rev. gen. Bot.	Revue generale de Botanique
Rev. gen. chim	Revue generale de chimie pure et appliquee (G. Jaubert)
Rev. gen lait	Revue generale du lait
Rev. gen mat. color.	Revue generale de matieres colorantes et de leurs applications aux textiles
Rev. gen sci.	Revue generale des sciences pure et appliquee
Rev. Hortic	Revue Horticole, Journal d'Horticulture pratique
Rev hyg. pol. sanitaire	Revue d'hygiene et de police sanitaire
Rev. Ind.	Revue Industrielle
Rev. Ind Chim.	Revue des industries chimiques et agricoles
Rev. Mag Zool	Revue et Magazine de Zoologie, pure et appliquee
Rev. Maritime Colon	Revue Maritime (et Coloniale)
Rev. Med Chir.	Revue Medico-Chirurgicale de Paris
Rev. Med Franc. Etrang.	Revue Medicale Française et Etrangere
Rev. Met.	Revue de Metallurgie
Rev. Mycol.	Revue Mycologique. Recueil trimestriel illustre consacre a l'Etude des Champignons
Rev. phot.	Revue de photographie
Rev. Quest Sci.	Revue des Questions scientifiques publiee par la Société Scientifique de Bruxelles
Rev. Sci.	(la) Revue Scientifique (de la France et de l'Etranger. Revue des Cours, Scientifiques)
Rev. Sci. Natur.	Revue des Sciences Naturelles
Rev. Soc. Hyg. Aliment.	Revue de la société scientifique d'Hygiene alimentaire et de l'alimentation rationnelle de l'homme
Rev. Suisse Zool.	Revue Suisse de Zoologie (et) Annales (de la Société Zoologique Suisse et) du Musee d'Histoire Naturelle de Geneve
Rev Univ. Mines	Revue universelle des Mines, de la Metallurgie, des Travaux Publics, des Sciences et des Arts Appliquee a l'Industrie. Annuaire de l'Association des Ingenieurs sortis de l'Ecole de Liege

Rev. Vit.	Revue Viticulture
Rev. Zool.	Revue Zoologique, par la Société Cuvierienne
Revista Brazil	Revista Brasileira, Journal de Ciencias, Lettras, e Artes
Revista, Chim. pure app	Revista de chimica pure applicada
Revista ind agric Tucuman	Revista industrial y agrocola de Tucuman
Revista Ligure	Revista Ligure, giornale di Lettere, Scienze, etc
Revista Med Chile	Revista medica de Chile
Revista Med. Cirug Habana	Revista de Medicina y Cirugia, Habana
Revista Minera	Revista Minera, periodico cientifico e industrial
Revista real acad cien Madrid	Revista de la real academia de ciencias de Madrid
Revista Telegr.	Revista de Telegrafos
Revista Trim. Microgr	Revista Trimestral Micrografica. Organo del Laboratorio Histologico de la Facultad de Medicina de Madrid
Rhea	Rhea, Zeitschrift fur die gesammte Ornithologie
Rhemische Monatsschr	Rheinische Monatsschrift fur praktische Aerzte
Rheinl Westphal	See Bonn
Rheinl Westphal Corresp	Correspondenzblatt des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinl Westphal Verh	Verhandlungen des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinl. Westphal Sitzber	Sitzungsbericht des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinpfalz Pollichia Festschr.	Festschrift zur Funfzigjahrigen Stiftungsfeier der Pollichia, Naturwissenschaftlichen Vereines der Rheinpfalz
Rheinpfalz Pollichia Jahr	Jahresbericht der Pollichia, eines Naturwissenschaftlichen Vereins der Rheinpfalz
Rheinpfalz Pollichia Mitth.	Mittheilungen der Pollichia, eines Naturwissenschaftlichen Vereins der Rheinpfalz
Rheinpfalz Pollichia Sep. Ausg.	.. Separat-Ausgabe der Pollichia, des Naturwissenschaftlichen Vereines der Pfalz
Rhodora	Rhodora. Journal of the New England Botanical Club
Riga, Arb Naturf Ver	Arbeiten des Naturforschenden Vereins in Riga
Riga, Corresp. Blatt. Naturf. Ver.	Correspondenz-Blatt, des Naturforschenden Vereins in Riga
Rio de Janeiro Archiv Palestr.	Archivos da Palestra Scientifica do Rio de Janeiro
Rio de Janeiro Mus Nac. Archiv.	Archivos do Museu Nacional do Rio de Janeiro
Rio de Janeiro Mus Nac Revista	Revista do Museu Nacional do Rio de Janeiro (Seguimento aos Archivos do Museu Nacional)
Rio de Janeiro Obs. Annaes	(Annaes do Imperial Observatorio do Rio de Janeiro)
Rio de Janeiro Obs Bol	Boletim mensal do Observatorio do Rio de Janeiro
Rio de Janeiro Obs Revista	Revista do Observatorio. Publicacao mensal do Imperial Observatorio do Rio de Janeiro
Rio, Revista	Revista tri mensal de Historia e Geographis: Journal do Instituto Historico e Geographico Brasileiro
Rio, Soc. Vell Trabal	Trabalhos da Sociedade Vellosiana (Bibliotheca Guanabarensis)
Riv.	Rivista
Riv. Bolognese	Rivista Bolognese di Scienze e Lettere
Riv. Geogr. Ital.	Rivista Geografica Italiana (e Bolletino della Societa di Studi Geografici e Coloniali in Firenze)



Riv. Ital. Sci. Natur. Napoli	Rivista Italiana di Scienze Naturali e loro Applicazioni pubblicata per cura degli Aspiranti Naturalisti
Riv. Ital. Sci. Natur. Siena	Rivista Italiana di Scienze Naturali e Bollettino del Naturalista Collettore, Allevatore, Coltivatore
Riv. Mat.	Rivista di Matematica
Riv. Mineral. Crist	Rivista di Mineralogia e Cristallografia Italiana
Riv. Patol. Veg.	Rivista di Patologia Vegetale
Riv. Sci.-Ind.	Rivista Scientifico-Industriale delle principali Scoperte ed Invenzioni fatte nelle Scienze e nelle Industrie
Riv. Sper. di Freniatria	Rivista Sperimentale di Freniatria e di Medicina legale
Riv. Vit. Ital.	Rivista di Viticoltura ed Enologia Italiana
Robin, J. Anat.	Journal de l'Anatomie et de la Physiologie normales et pathologiques de l'homme et des animaux
Rochelle	See under Charente-Inf.
Rochester Acad. Sci. Proc.	Proceedings of the Rochester New York Academy of Science
Rochester Trans. Elec. Med. Assoc.	Transactions of the National Electric Medical Associa- tion at its Third Meeting, at Rochester, U. S.
Rock Products	Rock Products
Rohr, Notizen	Notizen aus dem Gebiete der practischen Pharmacie
Rollett	See Graz.
Roma	See Congr. Med. Int. Atti, 1894
Roma, Atti Nuovi Lincei	Atti dell' Accademia Pontificia de' Nuovi Lincei
Roma, Atti Reale Accad.	Atti della Reale Accademia dei Lincei
Roma, Corresp. Sci.	Corrispondenza Scientifica in Roma per le avanza- mento delle Scienze, etc
Roma Ist. Bot. Annuario	Annuario del R. Istituto Botanico di Roma
Roma Lab. Anat. Norm. Ric.	Ricerche fatte nel Laboratorio di Anatomia Normale della R. Università di Roma
Roma, Nuovi Lincei Mem.	Memorie della Pontificia Accademia dei Nuovi Lincei
Roma, Oss. Coll. Rom. Mem.	Memorie del R. Osservatorio del Collegio Romano
Roma, R. Accad. Lincei (Roma), Soc. Ital. Mem.	Atti della R. Accademia dei Lincei Memorie di Mathematica e di Fisica della Società Italiana delle Scienze
Roma, Soc. Studi Zool. Boll.	Bollettino della Società Romana per gli Studi Zoologici
Roma, Specola Vaticana Pubbl.	Pubblicazioni della Specola Vaticana
Roma, Uff. Centr. Meteorol. Ann.	Annali dell' Ufficio Centrale di Meteorologia Italiana
Romer, Archiv Bot.	Archiv für die Botanik
Roser Wunderlich, Archiv	Archiv für physiologische Heilkunde. Continued as the Archiv d. Heilk.
Rotterdam Nieuwe Verh.	Nieuwe Verhandelingen van het Bataafsch Genoot- schap der Proefondervindelijke Wysbegeerte Rotterdam
Rouen, Bull. Soc. Emul.	Bulletins (des travaux) de la Société Libre d'Émula- tion de Rouen
Rouen, Soc. Sci. Bull.	Bulletin de la Société des Amis des Sciences Naturelles de Rouen
Rouen, Trav. Acad.	Precis analytique des Travaux de l' Academie des Sciences, Belles-Lettres, et Arts de Rouen
Roumanie Inst. Meteorol. Ann.	Annales de l'Institut Meteorologique de Roumanie
Roy. Engin. Papers	Annalele Institutului Meteorologic al Romaniei Papers on subjects connected with the duties of the Corps of Royal Engineers
Roy. Inst. J.	Journal of the Royal Institution of Great Britain

Roy. Inst. Proc.	Notices of the Proceedings at the Meetings of the Members of the Royal Institution of Great Britain, with Abstracts of the Discourses delivered at the Evening Meetings
Roy. School Naval Archit. Ann.	The annual of the Royal School of Naval Architecture and Marine Engineering
Roy. Soc. Proc.	Abstracts of the Papers printed in the Philosophical Transactions of the Royal Society of London, from 1800 to 1854 inclusive. Continued as the Proceedings of the Royal Society of London
Rugby, Natur Hist. Soc. Reports	Reports of the Rugby School Natural History Society
Russ. Annu. Geol. Mineral.	Russian Annual of Geology and Mineralogy
Russ. Annuaire Mines	Annuaire du Journal des Mines de Russie
Russ. Chem. Soc. J.	Journal of the Russian Chemical Society
Russ. Geogr. Ges. Denkschr.	Denkschriften der Russischen Geographischen Gesellschaft zu St. Petersburg
Russ. J. exp Landw.	Russisches Journal für experimentelle Landwirtschaft
Russ. Jahr. Pharm.	Russisches Jahrbuch der Pharmacie
Russ. P.	Russian Patent
Russ. Pharm. Zts	Pharmaceutische Zeitschrift für Russland
Russ. Phys.-Chem. Soc J.	Journal of the Russian Physico-Chemical Society of the Imperial University of St. Petersburg
Rust, Mag.	Magazin für die gesammte Heilkunde, etc.
S. Africa Chem. Metall. Soc.	The Journal of the Chemical and Metallurgical Society of South Africa
S. Africa Chem. Metall. Soc. Proc	The Proceedings of the Chemical and Metallurgical Society of South Africa
S. Africa. Mus. Ann.	Annals of the South African Museum
S. Africa. Phil. Soc. Trans.	The Transactions of the South African Philosophical Society
S. Austral. P.	South Australian Patent
S. Austral. Roy. Soc. Mem.	Memoirs of the Royal Society of South Australia
S. Austral. Roy. Soc. Trans.	Transactions and Proceedings and Report of the Royal Society of South Australia
S. C. Med. Assoc. Trans.	Transactions of the South Carolina Medical Association
S. London Entom. Natur. Hist. Soc. Proc.	(Abstract of) Proceedings of the South London Entomological and Natural History Society
S. Wales Inst. Civ. Engin. Proc.	Proceedings of the South Wales Institute of Civil Engineers
S. Wales Roy. Inst. Report	The annual report of the Council of the Royal Institution of South Wales, with Appendix of Original Papers on Scientific Subjects
Sächs. Ingen Ver. Mitth.	Mittheilungen des Sachsischen Ingenieur-Vereins; herausg. v. d. Verwaltungsrathe des Vereins
Sächs. Meteorol. Inst. Abh.	Abhandlungen des Königl. Sächs. Meteorologischen Institutes
Sachs. Thüring. Naturwiss. Ver.	See Zts. Naturwiss.
Salem	See Essex Institute
San Fernando Obs. Marina An.	Anales del Instituto y Observatorio de Marina de San Fernando
Sanitary Record	Sanitary Record and Journal of Municipal Engineering, The
Santiago Chile, Univ. Anales	(Republica de Chile.) Anales de la Universidad
Sao Paulo, Rev. Mus. Paulista	Revista do Museu Paulista

Saone-et-Loire Soc. Sci. Bull.	Bulletins de la Société des Sciences Naturelles de Saone-et-Loire
Saone-et-Loire Soc. Sci. Mem.	Memoires de la Société des Sciences Naturelle de Saone-et-Loire
Sarthe, Bull. Soc. Agric.	Bulletin de la Société d'Agriculture, Sciences, etc., de la Sarthe
Savoie Acad. Mem.	Memoires de l'Academie des Sciences, Belles-Lettres et Arts de Savoie
Savoie Soc. Hist. Natur. Bull.	Bulletins de la Société d'Histoire Naturelle de Savoie
Savoie Soc. Hist. Natur. (Compt. rend.)	Société d'Histoire Naturelle de Savoie a Chambéry
Schaffhausen	See Schweizer. Entom. Gesell
Scheik. Onderz.	See Utrecht Scheik Onderzoek
Schemnitz Bergakad.	See Wien, Berg- u. Huttenm. Jahr.
Scherer, J. Chem.	Allgemeines Journal der Chemie
Schlesw.-Holst. Naturwiss. Ver. Schr.	Schriften des Naturwissenschaftlichen Vereins für Schleswig-Holstein
Schlömilch, Zts.	Zeitschrift für Mathematik und Physik
Schneider, Ann. Staatsarz-neik.	Annalen der gesammten Staatsarzneikunde
School Mines Quart.	School of Mines, Quarterly, The
School of Mines, Records	Records of the School of Mines
Schrader, J. Bot.	Journal für die Botanik
Schroder, Berig. Zeevaart.	Berigten en Verhandelingen over eenige onderwerpen des Zeevaarts
Schröder, Verh. Zeevaart.	Verhandelingen en Berigten over eenige onderwerpen der Zeevaart-Kunde
Schuh Ind.	Schuh Industrie
Schumacher, Jahr.	Jahrbuch, (H. C. Schumacher, (1836-38))
Schwab. Ges. Denkschr.	Denkschriften der Schwabischen Gesellschaft der Aerzte und Naturforscher
Schwalbe	Ornithologische Section der k. k. Zoologisch-Botanischen Gesellschaft in Wien Die Schwalbe. Berichte des Comites für Ornithologische Beobachtungs-Stationen in Oesterreich
Schweigger, J. (Schw. J.)	Journal für Chemie und Physik
Schweiz. Alpenclub Jahr.	Jahrbuch des Schweizer Alpenclub
Schweiz. Bot. Ges. Ber.	Berichte der Schweizerischen Botanischen Gesellschaft
Schweiz. Entom. Ges. Mitth.	Mittheilungen der Schweizerischen Entomologischen Gesellschaft
Schweiz. Ges. Neue Denkschr.	Neue Denkschriften der allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften
Schweiz. Ges. Verh.	Verhandlungen der Schweizerischen Gesellschaft für die gesammten Naturwissenschaften
Schweiz. Monatsschr.	Schweizerische Monatsschrift für praktische Medizin
Schweiz. Naturf. Ges.	See Beitr. Kryptog. Schweiz.
Schweizer. Naturf. Ges. Verh.	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft
Schweiz. Phot.-Ver.	See Wien, Phot. Correspond.
Schweiz. Poly. Zts.	Schweizerische polytechnische Zeitschrift. Unter Mitwirkung des Schweizerischen Polytechnikums, etc.
Schweiz. Wochenschr.	Schweizerisch Wochenschrift für Chemie und Pharmacie
Schweiz. Zts. Heilk. Sci.	Schweizerische Zeitschrift für Heilkunde Science
Sci. Abst.	Science Abstracts. Physics and Electrical Engineering
Sci. Amer.	Scientific American

Sci. Amer. Suppl.	Scientific American Supplement
Sci. Can.	Scientific Canadian
Sci. Ind. Bull. Roure-Bertrand Fils	Scientific et Industrial Bulletin Roure-Bertrand Fils
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society
Sci. Rev.	The Scientific Review and Journal of the Inventors Institute
Sci. Trans. Roy. Dublin Soc.	Scientific Transactions of the Royal Dublin Society
Scienz. Ital. Congr.	Nuovo Congresso degli Scienziati Italiani in Venezia; porzione geologica
Slater, Ibis	The Ibis, a Magazine of General Ornithology
Scott. Arbor. Soc. Trans.	Transactions of the Scottish Arboricultural Society
Scott. Geogr. Mag.	The Scottish Geographical Magazine
Scott. Meteorol. Soc. J.	Journal of the Scottish Meteorological Society
Scott. Micro. Soc. Proc. & Trans.	Proceedings and Transactions of the Scottish Microscopical Society
Scott. Natur.	A Magazine of Scottish Natural History (and Journal of the Perthshire Society of Natural Science)
Scott. Soc. Arts Trans.	Transactions of the Royal Scottish Society of Arts
Seeman, J. Bot.	The Journal of Botany, British and Foreign
Seifenfabr.	Seifenfabrikant, Der
Seifens. Ztg.	Seifensieder Zeitung und Revue über die Harz, Fett und Oelindustrie
Seine (Dep. de la)	See (France) Soc. Agr. Mem.
Seine, Mem. Soc. Agric.	Memoires d'Agriculture par la Société Agricole de la Seine
Seine-et-Oise, Mem.	Memoires de la Société des Sciences Naturelles de Seine et Oise
Seism. J. Japan	Seismological Journal of Japan
Selenka, Archiv Zool.	Niederländisches Archiv für Zoologie
Semi-Ann. Rep. Schimmel & Co.	Semi-Annual Report, Schimmel & Co., Miltitz
Senckenberg. Naturf. Ges. Abh.	Abhandlungen herausg. von der Senckenbergischen Naturforschenden Gesellschaft
Senckenberg, Naturf. Ges. Ber.	Bericht über die Senckenbergische naturforschende Gesellschaft in Frankfurt am Main
Shanghai, J.	Journal of the North-China Branch of the Royal Asiatic Society
Shanghai, J. Lit. Soc.	Journal of the Literary and Scientific Society of Shanghai
Shoe Lea, Reporter	Shoe and Leather Reporter
Shropsh. Soc. Trans.	Transactions of the Shropshire Archaeological and Natural History Society
Sicilia, Atti Soc. Acclim.	Atti della Società di Acclimazione e di Agricoltura in Sicilia
Sidereal Messenger	The Sidereal Messenger
Siebenb. Karpath. - Ver. Jahr.	Jahrbuch des Siebenbürgischen Karpathen-Vereins
Siebold, J. Geburtshülfe	Journal für die Geburtshülfe, Frauenzimmer, etc., von Elias von Siebold
Siebold Kölliker, Zts.	Zeitschrift für wissenschaftliche Zoologie
Siebold, Lucina	Lucina; eine Zeitschrift zur Vervollkommen der Entbindungskunst
Siena, Atti Accad.	Atti dell' Accademia delle Scienze di Siena detta de' Fisiocritici
Silbermann, Rev. Entom.	Revue Entomologique

Silliman, J.	The American Journal of Science and Arts
Singapore Roy. Asiat. Soc	Journal of the Straits Branch of the Royal Asiatic Society. Singapore
J.	
Sitzber. kais. Akad. Wiss. Wien.	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, Wien (Mathematisch-naturwissenschaftliche Klasse) Abteilungen I, IIa, IIb, III
Sitzb. könig Akad. München	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München
Sitzber. könig. Akad. Wiss. Berlin	Sitzungsberichte der königlich preussischen Akademie der Wissenschaften zu Berlin
Sitzber. könig preuss. Akad	Sitzungsberichte der königlich preussischen Akademie der Wissenschaften
Skand Archiv Physiol.	Skandinavisches Archiv für Physiologie
Skand. Naturf. Forh.	Forhandlingar vid det af Skandinaviska Naturforskare och Lakare hållna Mote i Gotheborg
Skand Naturf. Mod. Forh.	Forhandlingerne ved de Skandinaviske Naturforskernes 11te Mode i Kjøbenhavn fra den 3die til den 9de Juli, 1873
Skand. Naturf. Möt. Forh.	Forhandlingar vid de Skandinaviska Naturforskarnes Tolfte Mote i Stockholm från den 7 till den 14 Juli, 1880
Skandia	Skandia Tidskrift för Vetenskap och Konst, utgifven af Svenska Litteratur-Föreningen
Skofitz	See Oesterreich Botan. Zeitschr
Skofitz, Bot. Wochenbl	Oesterreichisches Botanisches Wochenblatt
Skofitz, Bot. Zts	Oesterreichische Botanische Zeitschrift
Smithsonian Contrib	Smithsonian Contributions to Knowledge
Smithsonian Inst. Astro-phys. Obs. Ann.	Annals of the Astrophysical Observatory of the Smithsonian Institution
Smithsonian Inst. Bur. Ethnol. Report	Annual Report of the Bureau of (American) Ethnology to the Secretary of the Smithsonian Institution
Smithsonian Misc. Coll.	Smithsonian Miscellaneous Collections
Smithsonian Report	Annual Report of the Board of Regents of the Smithsonian Institution, showing the Operations, Expenditures and Condition of the Institution
Snelling's Phot. J.	Snelling's Photographisches Journal
Soc. Bot. Ital. Bull.	See Nuovo Giorn. Bot. Ital.
Soc. Broteriana	See Coimbra, Soc. Broter. Biol.
Soc. Elvet. Sci. Naturf. Atti	See Schweiz. Naturf. Ges. Verh.
Soc. Entom. Ross. Horae	Horae Societatis Entomologicae Rossicae variis sermonibus in Russia usitatis editae
Soc. Franc. Bot.	See Rev. Bot.
Soc. Franc. Entom.	See Rev. Ent.
Soc. Freniatr. Ital.	See Riv. Sper. di Freniatria
Soc. Geogr. Finland	See Fennia
Soc. Helvet. Actes	Actes de la Société Helvétique des Sciences Naturelles
Soc. Helvet. Sci. Naturf. Act.	See Schweiz. Natf. Ges. Verh.
Soc. Ital. Antrop.	See Arch. Antropologia
Soc. Ital. Fis.	See Nuovo Cimento
Soc. Ital. Micro. Boll.	See Acireale, Soc. Ital. Micr. Boll.
Soc. Ital. Sci.	See (Roma), Soc. Ital. Mem.
Soc. Ital. Sci. Nat.	See Milano, Soc. Ital.
Soc. Ligust. Sci. Naturf. Geogr.	See Genova, Soc. Ligust. Atti
Soc. Malacol. France	See Ann. Malacol.

Soc. Malacol. Ital. Bull.	See Bull. Malacol. Ital.
Soc. Meteorol. Ital.	See Moncalieri Oss. Boll.
Soc. Mex. Hist. Natur.	See Naturaleza
Soc. Napoli	Societa reale di Napoli. Rendiconto dell' Accademia delle Scienze fisiche e mathematiche
Soc. Nat. Sicil.	See Nat. Sicil.
Soc. Pharm. Anvers	See J. de Pharm.
Soc. Public Analysts	See Analyst
Soc. Speleol.	See Spelunca, Paris
Soc. Telegr.-Engin. Elect.	See Telegr. Eng. J.
Soc. Tosc. Sci. Nat.	See Pisa Soc. Tosc.
Soc. Ven.-Trent. Sci. Nat.	See Padova Soc. Sci.
Soc. Zool. Suisse Ann.	See Rev. Suisse: Zool.
Soc. Zool. Tokyo	See Annot. Zool. Jap.
Somerset. Archaeol. Soc. Proc.	Proceedings of the Somersetshire Archaeological and Natural History Society
Somerset. Sov. Proc.	Somersetshire Archaeological and Natural History Society's Proceedings
Somme (Dep. de la)	See under Amiens
Southern Pharm. J.	Southern Pharmaceutical Journal
Span. P.	Spanish Patent
Spatula	Saptula (The), Boston
Spelunca. Paris	Spelunca. Bulletin de la Société de Speleologie
Sperimentale	Lo Sperimentale. Giornale Italiano di Scienze Meidche
Spettatore Vesuvio	Lo Spettatore del Vesuvio e de' Campi Flegrei
Spettrosc. Ital. Mem.	Memorie della Societa degli Spettroscopisti Italiani
Spongia, Comm.-Med.	Commentari di Medicina
Sprechsaal	Sprechsaal
Sprengel, Jahr.	Jahrbucher der Gewachskunde
Sprengst. Waffen Mun.	Sprengstoffe, Waffen und Munition
St. Andrew's Med. Grad. Assoc. Trans.	Transactions of the St. Andrew's Medical Graduates Association
St Barthol. Hosp. Reports	St. Bartholomew's Hospital Reports
St. Etienne, Bull. Soc. Ind. Mineral	Bulletin de la Société de l'Industrie Minerale
St. Gallen, Ber. Naturwiss. Ges.	Berichte uber die Thatigkeit der St. Gallischen Naturwissenschaftlichen Gesellschaft
St. Louis, Bot. Gard. Report	Missouri Botanical Garden Report
St. Louis, Trans. Acad. Sci.	The Transactions of the Academy of Science of St. Louis
St. Petersb. Acad. Sci. Bull.	Bulletin scientifique publie par l'Academie Imperiale des Sciences de St. Petersburg
St. Petersb. Acad. Sci. Compt. rend.	Compte Rendu de l'Academie Imperiale des Sciences de St Petersburg
St. Petersb. Acad. Sci. Mem.	Memoires de l'Academie Imperiale des Sciences de St. Petersburg
St. Petersb. Acad. Sci. Nova Acta.	Nova Acta Academiae Scientiarum Imperialis Petropolitanae
St. Petersb. Acad. Sci. Recueil	Recueil des Actes des Seances Publiques de l'Academie Imperiale des Sciences de St. Petersburg
St. Petersb. Ann. Mines Russ.	Annuaire du Journal des Miner de Russie
St. Petersb. Archiv. Sci. Biol.	Archives des Sciences Biologiques publiees par l'Institut Imperial de Medecine Experimentale a St. Petersburg
St. Petersb., Congr. Bot. Bull.	Bulletin du Congres International de Botanique et d'Horticulture de St. Petersburg le 6/18, le 8/20 et le 10/22 Mai 1869

St. Petersb. Inst. Med. Exper.	See St. Petersburg Arch. Sci. Biol.
St. Petersburg Med. Zts.	St. Petersburg Medical Journal
St. Petersburg Med. Wochenschr.	St. Petersburg Medical Weekly
St. Petersburg. Mem. Savants Etrang.	Memoires presentes a l'Academie Imperiale des Sciences de St. Petersburg par divers Savants
St. Petersburg. Mineral. Ges. Verh.	Verhandlungen der Russisch-Kaiserlichen Mineralogischen Gesellschaft zu St. Petersburg
St. Petersburg, Russ. Geogr. Mem. (Geogr.)	Memoirs de la Société Imperiale Russe de Géographie
St. Petersburg, Russ. Geogr. Soc. Bull.	Section de Géographie générale
St. Petersburg. Schr. Mineral.	Bulletins of the Imperial Russian Geographical Society
St. Petersburg. Verh. Mineral. Ges.	Schriften der in St. Petersburg gestifteten Kaiserlich-Russischen Gesellschaft für die gesammte Mineralogie
St. Petersburg Verm. Abh.	Verhandlungen der Kaiserlich-Russischen Mineralogischen Gesellschaft zu St. Petersburg
St. Quentin, Ann.	Vermischte Abhandlungen aus dem Gebiete der Heilkunde von einer Gesellschaft pract. Aerzte zu St. Petersburg. Additional title in 1835, Medizinisch-praktische Abhandlung von Deutschen in Russland lebenden Aerzten. Continued as the Neue Abhandlung St. Petersburg
St. Quentin, Mem.	Annales Agricoles du département de l'Aisne, publiées par la Société des Sciences, Arts, Belles-Lettres, et Agriculture de St. Quentin. Annales Scientifiques, Agricoles, et Industrielles du département de l'Aisne (Société Académique de Saint Quentin)
St. Quentin, Seances Publ.	Memoires de la Société des Sciences, Arts, Belles-Lettres, et Agriculture de la ville de St. Quentin
St. Quentin, Travaux	Société des Sciences, Arts, Belles-Lettres, et Agriculture de la ville de St. Quentin. Seances publiques. Société Académique des Sciences, Arts, Belles-Lettres, et Agriculture de St. Quentin (Aisne)
St. Thomas's Hosp. Reports	Société Académique des Sciences, Arts, Belles-Lettres, et Agriculture de St. Quentin (Aisne)
Stahl Eisen (Zts.)	St. Thomas's Hospital Reports
Stavanger Mus. Aarsber.	Stahl und Eisen, Zeitschrift für das deutsche Eisenhüttenwesen
Staz. sper. agrar. ital.	Stavanger Museums Aarsberetning
Steiermark. Geog. Mont. Ver. Ber.	Stazioni sperimentali agraria italiana, La
Steiermark. Mitth.	Bericht des Geognostisch-montanistischen Vereins für Steiermark
Steiermark. Mont. Lehranst. Jahr.	Mittheilungen des Naturwissenschaftlichen Vereines für Steiermark
Stein, Ann.	Die Steiermarkisch-standische montanistische Lehranstalt zu Vordernberg
Stettin, Entom. Ztg.	Annalen der Geburtshilfe überhaupt und der Entbindungsanstalt zu Marburg insbesondere
Steyermark. Zts.	Entomologische Zeitung, herausg. v. d. Entomologischen Vereinen zu Stettin
Stirling Field Club Trans.	Steyermarkische Zeitschrift
Stirling Soc. Trans.	Stirling Field Club ... Transactions
Stockholm, Akad. Handl.	Stirling Natural History and Archaeological Society. Transactions
Stockholm, Bihang Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar
Stockholm Bot. Sallsk.	Bihang till Kongl. Svenska Vetenskaps Akademiens Handlingar
	See Bot. Centrbl.

Stockholm Entom. For.	See Ent. Tidskr.
Stockholm, Horti Bergiani Acta	Acta Horti Bergiani. Meddelanden från Kongl. Svenska Vetenskaps-Akademien Trädgård Bergielund utgifna af Bergianska Stiftelser
Stockholm, Öfversigt	Öfversigt af Kongl. Vetenskaps Akademien's Handlingar
Stockholm Physiol. Lab. Mitth	Mittheilungen vom Physiologischen Laboratorium des Carolinischen Medico-Chirurgischen Instituts in Stockholm
Stockholm, Svenska Lak. Sallsk. Handl.	Handlingar ved Svenska Lakare-Sällskapet
Stockholm, Vet. Akad. Lefnadsteckn.	Lefnadsteckningar öfver Kongl. Svenska Vetenskaps-Akademien efter år 1854 aflidna Ledamöter
Stockholm, Ymer	Ymer. Tidskrift utgifven af Svenska Sällskapet för Antropologi och Geografi
Strasbourg Soc. Hist. Natur. Mem.	Memoires de la Société du Museum d'Histoire Naturelle de Strasbourg
Strasbourg Soc. Sci. Bull.	Bulletin de la Société des Sciences Naturelles de Strasbourg
Strasbourg Soc. Sci. J.	Journal de la Société des Sciences, Agriculture, et Arts, du département du Bas-Rhin
Strasbourg Soc. Sci. Mem.	Memoires de la Société des Sciences, Agriculture, et Arts, de Strasbourg
Stray Feathers	Stray feathers. A journal of Ornithology for India and its dependencies
Stricker	See Medizin. Jahr.
Sts. Settl. P.	Straits Settlement Patent
Student	The Student and Intellectual Observer of Science, Literature, and Art
Sturgeon, Ann. Elect.	Annals of Electricity, Magnetism, and Chemistry, and Guardian of Experimental Science
Sturgeon, Ann. Phil.	Annals of Philosophical Discovery and Monthly Reporter of the Progress of Practical Science
Sucr.	La sucrerie indigene
Sucr. Belge	Sucrerie Belge, La
Sucr. ind. colon.	Sucrerie indigene et coloniale, La
Suddeut. Apoth. Ztg.	Süddeutsche Apotheker Zeitung
Suisse Soc. Zool. Ann.	See Rev. Suisse Zool.
Surveyor	Surveyor and Municipal and County Engineer, The
Sussex Natur. Hist. Soc. Proc.	See Brighton Nat. Hist. Soc. Proc.
Svea	Svea. Tidskrift för Vetenskap och Konst
Svensk farm. Tidskr.	Svensk farmaceutisk Tidskrift, Stockholm
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift
Svenska Lak. Sallsk. Forh.	Forhandlingar ved Svenska Lakare-Sällskapets Sammankomster
Svenska Mosskulturfor	Svenska Mosskulturforeningens
Svenska Sallsk. Antrop. & Geogr.	See Stockh., Ymer
Swart, Verh.	Verhandelingen en Berigten betrekkelijk het Zeewezen en de Zeewaartkunde
Swed. P.	Swedish Patent
Swiss P.	Swiss Patent
Sydney	See New South Wales
Sydney Aust. Mus. Mem.	The Australian Museum, Sydney. Memoirs
Sydney, Austral. Mus. Records	Records of the Australian Museum
Symons, Meteorol. Mag.	Symon's monthly Meteorological Magazine
Tablettes Zool.	Tablettes Zoologiques



Tagbl Frankf. Naturf.	Tageblatt Frankfurter Naturforscher
Taprobanian	The Taprobanian, a Dravidian Journal of Oriental Studies in and around Ceylon, in Natural History, Archaeology, Philology, History
Tasmania J. Natur. Sci	The Tasmanian Journal of Natural Science, Agriculture, Statistics, etc.
Tasmania P.	Tasmanian Patent
Tasmania, Roy. Soc.	Monthly Notices of Papers and Proceedings of the Royal Society of Tasmania
Monthly Not.	
Tasmania, Roy. Soc Re-ports	Reports of the Royal Society of Tasmania
Taylor, Sci Mem.	Scientific Memoirs, selected from the Transactions of Foreign Academies and Learned Societies and from Foreign Journals
Tech Blatter	Technische Blatter. Vierteljahrsschrift des Deutschen Polytechnischen Vereins in Bohmen
Tech. Chem Jahr.	Technisch-Chemisches Jahrbuch (Biedermann)
Tech Gemeindebl.	Technisches Gemeindeblatt
Technikum	Technikum des Ledermarkts
Technol	Le Technologiste (F Malepeyre)
Technol Quart.	Technology Quarterly
Teign Field Club Proc	Reports of the Proceedings of the Teign Naturalists' Field Club
Tekn Tidskr	Teknisk Tidskrift
Telegr Eng J.	Journal of the Society of Telegraph-Engineers and Electricians
Telegr J	The Telegraphic Journal and Electrical Review
Telegr Ver. Zts.	Zeitschrift des Deutsch-osterreichischen Telegraphen-Vereins
Temminck. Verh.	Verhandelingen over de natuurlijke Geschiedenis der Nederlandsche overzeesche bezittingen, door de leden der Natuurkundige Commissie in Oost-Indie en andere schrijvers
Termr. Fuz.	Termeszetráji Füzetek Kiadja a Magyar Nemzeti Múzeum (Natural History Magazine published by the Hungarian National Museum)
Termt. Közlön.	Termesztudományi Közöny. Kiadja a K. M. Termesztudományi Társulat. (Natural Science Papers. Published by the Royal Hungarian Natural Science Society)
Terrestrial Magn.	Terrestrial Magnetism (and Atmospheric Electricity). An International Quarterly Journal
Texas Acad. Sci. Trans	Transactions of the Texas Academy of Science
Text. Amer.	Textile American
Text. Col	The Textile Colorist
Text. Farb Ztg.	Textil und Färberei-Zeitung
Text. Mfr.	The Textile Manufacturer
Text. Rec	The Textile Record
Text. World Rec.	Textile World Record
Text Ztg.	Textil Zeitung
Textilfreund	Der Textilfreund
Teyler's Verh.	Geologische Verhandlung af Antwoord af de in 1828 uitgeschrevene en in 1830 herhaalde Pryspraak: Wat men van Geologie, etc.
Therap. Gaz.	The Therapeutic Gazette
Therap. Monats.	Therapeutische Monatshefte
Therap. Neuheit	Therapeutischen Neuheiten, Leipzig
Therapist	Therapist (The) London

Thomson, Ann. Phil.	Annals of Philosophy, or Magazine of Chemistry, Mineralogy, Mechanics, and the Arts
Thomson, Archiv. Entom.	Archives Entomologiques
Thomson, Rec.	Records of General Science
Thonind. Ztg.	Thonindustrie-Zeitung
Thronhjelm, Skrifter	Der Kongelige Norske Videnskabers-Selskabs Skrifter i det 19 de Aarhundrede
Tidskr. Kemi. Farm. Terapi	Tidsskrift for Kemi Farmaci Terapi
Tidskr. Mat.	Tidsskrift for Matematik
Tidskr. Mat. Fys.	Tidsskrift for Matematik och Fysik, tillegnad den Svenska Elementar-Undervisningen
Tidskr. Phys. Chem.	Tidsskrift for Physik og Chemi samt disse Videnskabers Anvendelse
Tiedemann, Zts.	Zeitschrift fur Physiologie
Tijdschr. Entom.	Tijdschrift voor Entomologie; uitgegeven door de Nederlandsche Entomologische Vereeniging
Tijdschr. Genootsch. Vis. Unita	Tijdschrift voor Genees-, Heel-, Verlos-, en Scheikundige Wetenschappen, van Wege et Genootschap: "Vis Unita Fortior," te Hoorn
Tijdschr. Ing.	Tijdschrift van het Koninklijk Instituut van Ingenieurs
Tijdschr. nijv.	Tijdschrift ter befordering van nijverheid
Tijdstroom.	De Tijdstroom, Maandschrift gewijd van Wetenschap, etc.
Tilesius, Jahr.	Jahrbuch der Naturgeschichte zur Anzeige und Prufung
Timehri	Timehri being the Journal of the Royal Agricultural and Commercial Society of British Guiana
Tirol, Ber. Ver. Durchf.	Bericht uber die General-Versammlung des Vereins zur geogr. montan. Durchforschung des Landes Tirol, etc.
Tischl. Ztg.	Deutsche Tischlerzeitung
Tokio Univ. Mem.	Memoirs of the Science Department, University of Tokio, Japan
Tokyo Bot. Soc.	See Bot. Mag., Tokyo
Tokyo, Coll. Sci. J.	The Journal of the College of Science, Imperial University, Japan
Tokyo Geogr. Soc. J.	Journal of the Tokio Geographical Society
Tonind. Ztg.	Tonindustrie Zeitung
Topfer Ztg.	Deutsche Topfer und Ziegler Zeitung
Torino, Accad. Sci. Atti	Atti della R. Accademia delle Scienze di Torino
Torino, Accad. Sci. Mem.	Memoire della R. Accademia delle Scienze di Torino
Torino, Ann. Clin	Annali Clinici
Torino, Lavori Sci. Fis. Mat.	Notizia storica dei lavori fatti dalla Classe di Scienze Fisiche e Matematiche della R. Accademia delle Scienze negli anni 1864-65
Torino Mus. Boll.	Bollettino dei Musei di Zoologia ed Anatomia comparata della R. Università di Torino
Torrey Bot. Club Bull.	Bulletin of the Torrey Botanical Club
Torrey Bot. Club Mem.	Memoirs of the Torrey Botanical Club
Tortolini, Ann.	Annali di Scienze, Matematiche, e Fisiche
Toulouse Acad. Sci. Bull.	Bulletin de l'Academie des Sciences, Inscriptions et Belles-Lettres de Toulouse
Toulouse, Acad. Sci. Mem.	Memoires de l'Academie des Sciences, Inscriptions et Belles-Lettres de Toulouse
Toulouse Fac. Sci. Ann.	Annales de la Faculte des Sciences de Toulouse, pour les Sciences Mathematiques et les Sciences Physiques
Toulouse Obs. Ann.	Annales de l'Observatoire Astronomique, Magnetique et Meteorologique de Toulouse.

Toulouse Soc. Hist. Natur Bull.	Bulletin de la Société d'Histoire Naturelle de Toulouse
Toulouse Soc Sci. Bull.	Bulletin de la Société des Sciences Physiques et Naturelles de Toulouse
Trans. Acad Sci St. Louis	Transactions of the Academy of Sciences of St. Louis
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society
Trans. Amer. Electrochem. Soc	Transactions of the American Electrochemical Society
Trans Amer. Inst. Chem Eng.	Transactions of the American Institute of Chemical Engineers
Trans. Amer. Inst. Homoeop	Transactions of the American Institute of Homoeopathy, Philadelphia
Trans. Amer. Inst Min Eng	Transactions of the American Institute of Mining Engineers
Trans. Amer. Med. Assoc Sec Pharm Therap.	Transactions of the Section on Pharmacology and Therapeutics of the American Medical Association
Trans Amer Micro. Soc	Transactions of the American Microscopical Society
Trans Amer Soc. Civ. Eng	Transactions of the American Society of Civil Engineers
Trans Cambr Phil Soc	Transactions of the Cambridge Philosophical Society
Trans Can Inst.	Transactions of the Canadian Institute
Trans Engl Ceram Soc	Transactions of the English Ceramic Society
Trans. Faraday Soc	Transactions of the Faraday Society
Trans Geol Soc. S Africa	Transactions of the Geological Society of South Africa
Trans. Illum Eng Soc.	Transactions of the Illuminating Engineering Society
Trans. Inst Brew.	Transactions of the Institute of Brewing
Trans. Jenner Inst Prev. Med	Transactions of the Jenner Institute of Preventive Medicine
Trans Kansas Acad Sci.	Transactions of the Kansas Academy of Science
Trans Med	Transactions Medicales, Journal de Medecine pratique
Trans Min Geol. Inst India	Transactions of the Mining and Geological Institute of India
Trans Natl. Eclec. Med. Assoc	Transactions National Eclectic Medical Association Indianapolis
Trans Nova Scotia Inst. Sci	Transactions of the Nova Scotia Institute of Science
Trans v P	Transvaal Patent
Trans Path. Soc.	Transactions of the Pathological Society
Trans Roy Irish Acad	Transactions of the Royal Irish Academy
Trans Roy Soc. Can	Transactions of the Royal Society of Canada
Trans Roy Soc. Edmb.	Transactions of the Royal Society of Edinburgh
Trans. Roy Soc London	Transactions of the Royal Society of London
Trans. Soc Engin	Society of Engineers, Transactions
Trav. Com. Hyg. Publ.	Recueil des Travaux du Comité consultatif d'Hygiène Publique de France et des Actes Officiels de l'Administration Sanitaire
Trenton Natur Hist. Soc J.	Journal of the Trenton, New Jersey, Natural History Society
Treviso, Mem. Ateneo	Memorie Scientifiche e Letterarie dell' Ateneo di Treviso
Trier, Jahr.	Jahresbericht der Gesellschaft für nützliche Forschungen zu Trier
Triest Zool Sta Arb.	See Wien Zool. Inst. Arb.
Trieste, Boll.	Bollettino della Società Adriatica di Scienze Naturali in Trieste
Trieste Mus Civ. Atti	Atti del Museo Civico di Storia Naturale di Trieste
Trieste, Program. Civ. Scuola	Programma della Civica Scuola Reale autonoma in Trieste

Trinidad Field Natur. Club J.	Journal of the Trinidad Field Naturalists' Club
Trinidad P.	Trinidad Patent
Trinidad, Proc. Sci. Assoc.	Proceedings of the Scientific Association of Trinidad
Trinidad, Sci. Assoc. Proc.	Proceedings of the Scientific Association of Trinidad
Trommsdorff, J. Pharm.	Journal der Pharmacie fur Aerzte und Apotheker, und Chemiker
Tromso. Mus. Aarsh.	Tromso Museums Aarshefter
Tropenpflanzer	Tropenpflanzer (Der), Berlin
Tsch. Mineral. Mitth.	Tschermak's Mineralogische Mitteilungen
Tuberculosis	Tuberculosis. The Journal of the National Association for the Prevention of Consumption and other forms of Tuberculosis
Tubinger Blätter	Tubinger Blatter fur Naturwissenschaften und Arzneikunde
Tubingen Bot. Inst. Unters.	Untersuchungen aus dem Botanischen Institut zu Tubingen
Tunis P.	Tunis Patent
Turin, Mem. Acad.	Memoires de l'Academie Royale des Sciences de Turin
Tyneside Natur. Field Club Trans.	Transactions of the Tyneside Naturalist's Field Club
U. K. Mar. Biol. Assoc. J.	Journal of the Marine Biological Association of the United Kingdom
U. S. Bur. Anim. Ind. Bull.	U. S. Department of Agriculture. Bureau of Animal Industry
U. S. Bur. Anim. Ind. Report	Annual Report of the Bureau of Animal Industry
U. S. Chief Signal Off. Ann. Report	Annual Report of the Chief Signal Officer (of the Army) to the Secretary of War
U. S. Coast Geod. Surv. Bull.	United States Coast and Geodetic Survey. Bulletin
U. S. Comm. Agric. Report	Report of the Commissioner of Agriculture
U. S. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U S
U. S. Dept. Agric. Report	Reports of the Department of Agriculture, U S
U. S. Dept. Agric. Yearb.	Yearbook of the United States Department of Agriculture
U. S. Disp.	United States Dispensatory
U. S. Div. Biol. Surv. Bull.	U. S. Department of Agriculture. Division of Biological Survey. Bulletin
U. S. Div. Chem. Bull.	U. S. Department of Agriculture. Division of Chemistry. Bulletin
U. S. Div. Entom. Bull.	U. S. Department of Agriculture. Division of Entomology
U. S. Div. Entom. Insect Life	U. S. Department of Agriculture. Division of Entomology. (Periodical Bulletin) Insect Life
U. S. Div. Entom. Tech. Ser.	U. S. Department of Agriculture. Division of Entomology. Technical Series
U. S. Div. Ornith. Mamm. Bull.	U. S. Department of Agriculture. Division of Economic Ornithology and Mammalogy. Bulletin
U. S. Div. Soils Bull.	U. S. Department of Agriculture. Division of (Agricultural) Soils. Bulletin
U. S. Entom. Comm. Bull.	Department of the Interior... Bulletin of the United States Entomological Commission
U. S. Entom. Comm. Report	(U. S.) Department of the Interior (Agriculture)... Report of the United States Entomological Commission
U. S. Fish Comm. Bull.	Bulletin of the United States Fish Commission
U. S. Fish Comm. Report	United States Commission of Fish and Fisheries. Report of the Commissioner

U. S. Geol. Surv.	United States Geological Survey
U. S. Monthly Weath. Rev.	(United States) Monthly Weather Review
U. S. Mus. Bull.	Department of the Interior... Bulletin of the United States National Museum
U. S. Mus. Proc.	Department of the Interior... Proceedings of the United States National Museum
U. S. Mus. Report	See Smithsonian Rep.
U. S. Mus. Spec. Bull.	Smithsonian Institution United States National Museum. Special Bulletin
U. S. Naval Inst. Proc.	United States Naval Institute Proceedings
U. S. Naval Med. Bull.	United States Naval Medical Bulletin
U. S. Naval Obs. Publ.	Publications of the United States Naval Observatory
U. S. N. Amer. Fauna	U. S. Department of Agriculture. Division of Ornithology and Mammalogy. North American Fauna
U. S. P.	United States Patent
U. S. Ph.	United States Pharmacopoeia
U. S. Secty. Agric. Report	Report of the secretary of agriculture
U. S. Signal Serv. Notes	United States of America. War Department. Signal Service Notes
U. S. Signal Serv. Pap.	United States of America, War Department. Professional Papers of the Signal Service
U. S. Surv. Terr. Reports	...Annual Report of the United States Geological (and Geographical) Survey of the Territories
U. S. Weath. Bur. Bull.	U. S. Department of Agriculture. Weather Bureau. Bulletin
U. S. Weath. Bur. Report	U. S. Department of Agriculture Weather Bureau. Report of the Chief of the Weather Bureau
U. Serv. Inst. J.	Journal of the royal United Service Institution, Whitehall Yard
Udine, Relazioni	Relazioni intorno agli Atti dell' Accademia di Udine
Uhland's Tech. Rund.	Uhland's Technische Rundschau
Umschau	Umschau, Die
Ung. Naturwiss. Ver. Jahr.	Abhandlungen aus dem dritten Bande der Jahrbucher des Ungarischen naturwissenschaftlichen Vereins zu Pest, in Deutscher Uebersetzung Red. von J. Szabo
Univ. Ill. Bull.	University of Illinois Bulletin
Unters. Naturlehre	Untersuchungen zur Naturlehre des Menschen und der Thiere
Upsala, Arsskrift	Universitets Arsskrift utgifven af Kongl. Vetenskaps-Societeten i Upsala
Upsala Bot. For.	See Bot. Notiser
Upsala, Diss. Acad.	Dissertationes Academicæ Upsaliæ habitæ
Upsala, Frey Tidskr.	Frey Tidskrift for Vetenskap och Konst
Upsala Läkareför. Förh.	Upsala Läkareforenings Förhandlingar
Upsala Naturvet. Student-sällsk.	See Bot. Centrbl.
Upsala, Soc. Sci. Nova Acta	Nova Acta Regiæ Societatis Scientiarum Upsaliensis
Urug. P.	Uruguay Patent
Utrecht, Aanteek. Prov. Genoots.	Aanteekeningen van het Verhandelde in de Sectie-Vergaderingen van het Provinciaal Utrechtsch Genootschap van Kunsten en Wetenschappen
Utrecht, Ann. Acad.	Annales Academiæ Rheno-Trajectinæ
Utrecht, Kliniek	Kliniek: Tijdschrift voor Wetenschappelijke Geneeskunde
Utrecht, Nieuwe Verh. Prov. Genootsch.	Nieuwe Verhandelingen van het Provinciaal Utrechtsch Genootschap van Kunsten en Wetenschappen

Utrecht, Onderzoek.	Onderzoekingen gedaan in het Physiologisch Laboratorium der Utrechtsche Hoogeschool
Utrecht, Scheik. Onderzoek.	Scheikundige Onderzoekingen, gedaan in het Laboratorium der Utrechtsche Hoogeschool
Utrecht, Verh. Prov. Genootsch.	Verhandelingen van het Provinciaal Utrechtsch Genootschap van Kunsten en Wetenschappen
Valais Soc Murith.	See Bull. Murith
Valencia, Act. Med.	Actas del Instituto Medico Valenciano
Valenciennes, Mem. Soc. Agric.	Memoires de la Société d'Agriculture, des Sciences, et des Arts, de l'Arrondissement de Valenciennes
Valentin, Rep.	Repertorium für Anatomie und Physiologie
Van Diemen's Land, Roy. Soc. Papers	Papers and Proceedings of the Royal Society of Van Diemen's Land
Van Diemen's Land, Roy. Soc. Reports	Reports of the Royal Society of Van Diemen's Land (For Horticulture, Botany, and the Advance of Science)
Van Nostrand's Mag.	Van Nostrand's Engineering Magazine
Vargasia	Vargasia Boletín de la Sociedad de Ciencias físicas y naturales de Caracas
Varsovie Soc Natur. Trav.	Comptes Rendus et Memoires de la Société des Naturalistes (à l'Université Impériale) de Varsovie
Varsovie Soc. Natur. Trav. (Mem.)	Travaux de la Société des Naturalistes de l'Université Impériale de Varsovie
Vaucluse Acad. Mem.	Memoires de l'Académie de Vaucluse
Venez. P.	Venezuela Patent
Venezia, Ateneo	L'Ateneo Veneto: Rivista mensile di Science, Lettere ed Arti
Venezia, Ateneo Esercit.	Esercitazioni Scientifiche e Letterarie dell' Ateneo di Venezia
Venezia, Atti	Atti delle Adunanze dell' I. R. Istituto Veneto di Scienze, Lettere, ed Arti
Venezia, Atti Ateneo	Atti dell' Ateneo Veneto
Venezia, Iat. Atti	Atti del Reale Istituto Veneto di Scienze, Lettere ed Arti
Venezia, Ist. Mem.	Memorie del Reale Istituto Veneto di Scienze, Lettere ed Arti
Venezia, Mem. Ist. Beneto	Memorie dell' I. R. Istituto Veneto di Scienze, Lettere, ed Arti
Ver. Anal. Chem.	See Repert. Anal. Chem.
Verh. Genootsch. Occ. Qui Non	Verhandelingen van het Genootschap: "Occidit qui qui non servat"
Verh. Ges. deut. Naturf. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte
Verh. poly. Ges.	Verhandlungen der polytechnischen Gesellschaft
Verh. Ver. Gewerbeleis.	Verhandlungen des Vereins zur Beförderung des Gewerbeleisses in Preussen
Veröffent. kais. Gesundh.	Veröffentlichungen des kaiserlichen Gesundheitsamts
Verona, Soc. Ital. Mem.	Memorie di Matematica e Fisica della Società Italiana della Scienze
Vet. J. London	Veterinary Journal, London
Vet. Med. Assoc. Trans. Veterinarian	Transactions of the Veterinary Medical Association The Veterinarian
Victoria Dept. Mines Spec. Reports	Victoria. Department of Mines. Special Reports
Victoria Field Natur. Club	See Victorian Natlist.
Victoria Inst. J.	Journal of the Transactions of the Victoria Institute or Philosophical Society of Great Britain
Victoria Natur.	The Victorian Naturalist. The Journal and Magazine of the Field Naturalists' Club of Victoria

Victoria P.	Victoria Patent
Victoria Pharm. Soc. J.	Quarterly Journal and Transactions of the Pharmaceutical Society of Victoria
Victoria Proc. Roy. Soc.	Proceedings of the Royal Society of Victoria
Victoria Trans. Phil. Inst.	Transactions of the Philosophical Institute (afterwards Royal Society) of Victoria
Victoria Trans. Roy. Soc.	Transactions of the Royal Society of Victoria
Victoria Zool. Soc. Proc.	Proceedings of the Zoological and Acclimatisation Society of Victoria
Vierteljahrschr. ärzt. poly.	Vierteljahrschrift der ärztlichen Polytechnik
Vierteljahrschr. gericht. Med.	Vierteljahrschrift für gerichtliche Medizin und öffentliches Sanitätswesen
Vierteljahrschr. gesundheitspf.	Vierteljahrschrift für Gesundheitspflege
Vierteljahrschr. Zahnheilk.	Vierteljahrschrift für Zahnheilkunde
Virchow's Archiv path.	Virchow's Archiv für pathologie, Anatomie, und Histologie
Viviani, Ann Bot.	Annali di Botanica
Voget, Notizen	Notizen aus dem Gebeite der practischen Pharmacie
Voigt, Mag.	Magazin für den neuesten Zustand der Naturkunden, mit Rücksicht auf die dazu gehorigen Hulfswissenschaften
Vosges Soc. Emul. Ann.	Annales de la Société d'Émulation du Department des Vosges
W. Austral. P.	West Australian Patent
Wag. Free Inst. Sci. Trans	Transactions of the Wagner Free Institute of Science of Philadelphia
Wag. Jahr	(Wagner's) Jahresbericht über Chemische Technologie
Walker, Elect. Mag.	The Electrical Magazine
Warwick. Field Club Proc.	Proceedings of the Warwickshire Naturalists' and Archaeologists' Field Club
Warwick Natur Hist. Soc. Rep	Annual Reports of the Warwickshire Natural History and Archaeological Society
Washburn Obs. Publ.	Publications of the Washburn Observatory of the University of Wisconsin
Washington	Int. Med Congr Trans, 1887
Washington	See also under U. S.
Washington Biol. Soc. Proc.	Proceedings of the Biological Society of Washington
Washington, Mem. Natl. Acad.	Memoirs of the National Academy of Sciences
Washington, Natl. Inst. Bull.	Bulletin of the Proceedings of the National Institution for the Promotion of Science
Washington Phil. Soc. Bull.	Bulletin of the Philosophical Society of Washington
Wasser Abwasser	Wasser und Abwasser
Water Supply Papers	Water Supply Papers
Watford Nat. Hist. Soc. Trans.	Transactions of the Watford Natural History Society and Hertfordshire Field Club
Weale, Quart. Papers	Quarterly Papers on Engineering
Weber, Archiv	Archiv für die systematische Naturgeschichte
Weimer, Zts. Geburtsk.	Gemeinsame Deutsche Zeitschrift für Geburtskunde
Weinlaube	Die Weinlaube
Wernigerode Naturwiss. Ver. Schr.	Schriften des Naturwissenschaftlichen Vereins des Harzes in Wernigerode
West. Brewer	Western Brewer, The
West. Chem. Met.	Western Chemist and Metallurgist
West. Drug.	Western Druggist

Westphäl. Prov. Blatt.	Westphalische Provincial-Blätter. Verhandlungen der Gesellschaft zur Beförderung der vaterländischen Cultur in Minden
Westphäl. Ver. Jahr.	Jahres-Bericht des Westfälischen Provinzial-Vereins für Wissenschaft und Kunst
Wetter	Das Wetter. Meteorologische Montasschrift für Gebildete aller Stände
Wetterau. Ges. Ann.	Annalen der Wetterauischen Gesellschaft für die gesammte Naturkunde
Wetterau. Ges. Festgabe.	Naturhistorische Abhandlungen aus dem Gebiete der Wetterau
Wetterau. Ges. Jahr.	Jahresbericht der Wetterauischen Gesellschaft für die gesammte Naturkunde
Wetterau. Ges. Naturk. Ber.	Bericht der Wetterauischen Gesellschaft für die gesammte Naturkunde zu Hanau
Wiad. Mat.	Wiadomości Matematyczne
Wieck's Gewerbeztg.	Deutsche Gewerbezeitung (F. Wieck)
Wied. Ann. Phys.	Annalen der Physik und Chemie (Wiedemann's)
Wied. Archiv	Archiv für Zoologie und Zootomie
Wied. Zool. Mag.	Zoologisches Magazin
Wiegmann, Archiv	Archiv für Naturgeschichte
Wien Abh.	Naturwissenschaftliche Abhandlungen
Wien Akad. Ber.	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften; Mathematisch-Naturwissenschaftliche Klasse, II Abthlg. Wien
Wien Akad. Denkschr.	Denkschriften der kaiserlichen Akademie der Wissenschaften. Mathematisch - Naturwissenschaftliche Classe
Wien Akad. Sitzber.	Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Classe der kaiserlichen Akademie der Wissenschaften
Wien Almanach	Almanach der kaiserlichen Akademie der Wissenschaften
Wien Alpen-Verein, Jahr.	Jahrbuch des Oesterreichischen Alpen-Vereins
Wien Anthropol. Ges. Mitth.	Mittheilungen der Anthropologischen Gesellschaft
Wien Anz.	Anzeiger der kaiserlichen Akademie der Wissenschaften Math.-Naturwissensch. Classe
Wien Denkschr.	Denkschriften der kaiserlichen Akademie der Wissenschaften. Mathematisch - naturwissenschaftliche Classe
Wien Embryol. Inst. Mitth.	Mittheilungen aus dem Embryologischen Institute der k. k. Universität in Wien
Wien Geogr. Ges. Abh.	Abhandlungen der k. k. Geographischen Gesellschaft in Wien
Wien Geogr. Ges. Festschr.	Festschrift der k. k. Geographischen Gesellschaft 1884-1898
Wien Geogr. Ges. Mitth.	Mittheilungen der k. k. Geographischen Gesellschaft in Wien
Wien Med. Chir. Acad. Abh.	Abhandlungen der k. k. medicinisch-Chirurgischen Josephs-Academie zu Wien
Wien Med. Chir. Acad. Beob.	Beobachtungen der k. k. medicinisch-chirurgischen Josephs-Academie zu Wien
Wien Naturhist. Hofmus. Ann.	Annalen des k. k. Naturhistorischen Hofmuseums
Wien Ornith. Vrr. Mitth.	Mittheilungen des Ornithologischen Vereins in Wien
Wien Phot. Corresp.	Photographische Correspondenz. Organ der Photograph. Gesellsch. in Wien
Wien Schr.	Schriften des Vereines zur Verbreitung naturwissenschaftlicher Kenntnisse



Wien Sitzber.	Sitzungsberichte der Mathematisch-naturwissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften
Wien, Sonnblick-Ver. Jahr.	Jahres-Bericht des Sonnblick-Vereines Wien
Wien. technol. Blätter	Wiener technologische Blätter
Wien Ver Naturwiss Kennt. Schr	Schriften des Vereins zur Verbreitung naturwissenschaftlicher Kenntnisse in Wien
Wien, Ver. Ges. Aerzte.	Verhandlungen der k. k. Gesellschaft der Aerzte zu Wien
Wien Verh. Gewerb-Vereins	Verhandlungen des Neiderösterreichischen Gewerb-Vereins
Wien Wochenbl Aerzte	Wochenblatt der k. k. Gesellschaft der Aerzte in Wien
Wien Zts. Ges. Aerzte	Zeitschrift der k. k. Gesellschaft der Aerzte zu Wien
Wien, Zool. Bot. Ges. Festschr.	Festschrift zur Feier des funfundzwanzigjährigen Bestehens der k. k. Zoologisch-Botanischen Gesellschaft in Wien
Wien, Zool. Bot. Verh.	Verhandlungen der k. k. Zoologisch-Botanischen Gesellschaft in Wien
Wien, Zool. Inst. Arb.	Arbeiten aus dem Zoologischen Institute der Universität Wien und der Zoologischen Station in Triest
Wiener Entom. Monatschr.	Wiener Entomologische Monatschrift
Wiener Entom. Ver. Jahr.	Jahresbericht des Wiener Entomologischen Vereins
Wiener Entom. Ztg.	Wiener Entomologische Zeitung
Wiener klin. Wochenschr.	Wiener klinische Wochenschrift
Wiener landw. Ztg.	Wiener landwirtschaftliche Zeitung
Wiener Med. Wochenschr.	Wiener medicinische Wochenschrift
Wiener Mitth. Phot.	Wiener Mittheilungen (Photographischen Inhalts)
Wiener Mus. Ann.	Annalen des Wiener Museums der Naturgeschichte
Wiener Poly. J.	Allgemeines Wiener polytechnisches Journal
Wiener Ztg.	Wiener Zeitung
Wiener Zts. Physik	Zeitschrift für Physik, Chemie, und Mineralogie
Wild, Rep. Meteorol	Repertorium für Meteorologie, herausg. von der kaiserlichen Akad. der Wissenschaften
Wilna, Collect. Med. Chir.	Collectanea medico-chirurgica Caesarea Academiae Medico-Chirurgicae cura edita
Wilts, Archæcol. Natur Hist. Mag.	Magazine of the Archaeological and Natural History Society of Wiltshire
Wimereux Lab. (Stat.) Zool.	See Lille Inst. Zool. Trav.
Winchester, J. Sci. Soc.	Journal of Proceedings and Annual Reports of the Winchester and Hampshire Scientific and Literary Society
Wisconsin Acad. Trans.	Transactions of the Wisconsin Academy of Sciences, Arts, & Letters
Wisconsin Natur. Hist. Soc. Bull.	Bulletin of the Wisconsin Natural History Society
Wisconsin Natur. Hist. Soc. Pap.	Occasional Papers of the Natural History Society of Wisconsin
Wisconsin Natur. Hist. Soc. Proc.	Proceedings of the Natural History Society of Wisconsin
Wisconsin Univ. Bull. Sci.	Bulletin of the University of Wisconsin Science Series
Wiss. Abh. Phys.-Tech. Reichsanstalt	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt
Wiss. Meeresuntersuch.	Wissenschaftliche Meeresuntersuchungen herausgegeben von der Kommission zur wissenschaftlichen Untersuchung der deutschen Meere in Kiel und der biologischen Anstalt auf Helgoland

Wochenbl. Archit. Ver.	Wochenblatt, herausgegeben von mitgliedern des Architekten-Vereins zu Berlin
Wochenbl. Papierfabr.	Wochenblatt der Papierfabriken
Wochensch. Brau.	Wochenschrift für Brauerei
Wochenschr. Centr.-Ver. Rubezucker-ind.	Wochenschrift des Central-Vereins für Rubenzucker-industrie in der Oesterr.-Ung.-Monarchie
Wochenschr. osterr. Ing. Ver.	Wochenschrift des österreichischen Ingenieur und Architekten Vereins
Wochenschr. Ver. deut. Ing.	Wochenschrift des Vereins deutscher Ingenieure
Wollen-Gewerbe	Das Deutsche Wollen-Gewerbe
Wollen Ztg.	Wollen Zeitung
Wombat	The Wombat. The Journal of the Geelong Field Naturalists' Club, and the Gordon College Amateur Photographic Association
Woods Holl Mar. Biol. Lab. Bull.	Biological Bulletin. Edited by the Director and Members of the Staff, of the Marine Biological Laboratory, Woods Holl, Mass.
Woods Holl Mar. Biol. Lab Lect.	Biological Lectures delivered at (from) the Marine Biological Laboratory (of) Woods Holl (Mass.)
Woolhope Field Club Trans	Transactions of the Woolhope Naturalists' Field Club
Woolwich, Proc.	Minutes of Proceedings of the Royal Artillery Institution
World's Paper Trade Rev.	World's Paper Trade Review
Wunderlich, Archiv. Heilk.	See Roser und Wunderlich
Wurtemberg. Aerzt. Ver. Mitth	Mittheilungen des Württembergischen Aerztlichen Vereins
Wurtemberg, Jahresh.	Jahreshefte des Vereins für vaterländische Naturkunde in Württemberg
Wurzburg, Arb Bot. Inst.	Arbeiten des Botanischen Instituts in Würzburg
Wurzburg, Arb Phys. Lab	Arbeiten aus dem Physiologischen Laboratorium der Würzburger Hochschule
Wurzburg. Med. Zts.	Würzburger medicinische Zeitschrift
Wurzburg. Naturwiss. Zts.	Würzburger Naturwissenschaftliche Zeitschrift; Herausgegeben von der Physikalisch-Medicinischen Gesellschaft
Wurzburg Phys. Med. Festschr.	Festschrift zur Feier ihres funfzigjahreign Bestehens herausgegeben von der Physikalisch-Medicinischen Gesellschaft zu Würzburg
Wurzburg, Phys. Med. Sitzber.	Sitzungsberichte der Physikalisch-Medicinischen Gesellschaft zu Würzburg
Wurzburg, Phys. Med. Verh.	Verhandlungen der Physikalisch-Medicinischen Gesellschaft
Wurzburg, Zool Inst. Arb.	Arbeiten aus dem Zoologisch-Zootomischen Institut in Würzburg
Year Book Pharm.	See Brit Pharm. Confer. Proc.
Year-book of Pharm.	Year-book of Pharmacy
Yn Lloar Manninagh	Yn Lloar Manninagh. The Journal of the Isle of Man Natural History and Antiquarian Society
Yokohama, Mitth. Deut. Ges.	Mittheilungen der Deutschen Gesellschaft für Natur und Volkerkunde Ostasiens
Yonne	See Auxere
Yonne, Bull.	Bulletin de la Société des Sciences Historiques et Naturelles de l'Yonne
Yorksh. Natur. Union Trans.	The Transactions of the Yorkshire Naturalists' Union
Yorksh. Phil. Soc. Report	Annual Report of the Council of the Yorkshire Philosophical Society

Yorksh. Proc. Phil. Soc	Proceedings of the Yorkshire Philosophical Society
Zach, Corresp.	Correspondence Astronomique, Geographique, Hydrographique, et Statistique
Zach, Monat. Corresp.	Monatliche Correspondenz zur Beförderung der Erd- und Himmels-Kunde
Zahntech.	Die Zahntechnische Reform
Zantedeschi, Ann. Fis.	Annali di Fisica
Zeeuwsch Genootsch.	Nieuwe Verhandelingen van het Zeeuwsch Genootschap der Wetenschappen
Nieuwe Verh	
Zeeuwsch Genootsch. Wet.	Archief Vroegere en Latere Mededeelingen voornamelijk in Betrekking tot Zeeland, uitgegeven door het Zeeuwsch Genootschap der Wetenschappen
Archief	
Zentr. Biochem. Biophys.	Zentralblatt für Biochemie und Biophysik
Zentr. exp. Med.	Zentralblatt der experimentellen Medizin (former name Zentralblatt für die gesamte Physiologie und Pathologie des Stoffwechsels)
Zentr. inn. Med.	Zentralblatt für innere Medizin
Zentr. oesterr - ungar	Zentralblatt für die oesterr-ungar Papierindustrie
Papierind.	
Zentr. Physiol.	Zentralblatt für Physiologie
Zentr. Physiol. Path. Stoffwech.	Zentralblatt für die gesammte Physiologie und Pathologie des Stoffwechsels, Berlin und Wien
Zeuner, Civilingenieur	Der Civilingenieur, Zeitschrift für das Ingenieurwesen
Ziva	Ziva. Casopis prirodnický
Zool. Anz.	Zoologischer Anzeiger
Zool. Beitr.	Zoologische Beiträge
Zool. Bull.	Zoological Bulletin
Zool. Congr.	See Congr. Int. Zool. C. R. Int. Congr. Zool. Proc.
Zool. Jahr.	Zoologische Jahrbücher. Zeitschrift für Systematik, Geographie und Biologie der Thiere
Zool. J.	The Zoological Journal
Zool. Soc. Proc.	Proceedings of the Scientific Meetings (General Meetings for Scientific Business) of the Zoological Society of London
Zool. Soc. Trans.	Transactions of the Zoological Society of London
Zool. Vortr.	Zoologische Vorträge
Zoologica	Zoologica. Original-Abhandlungen aus dem Gesamtgebiete der Zoologie
Zoologist	The Zoologist; a monthly Journal of Natural History
Ztg. Blechind.	Illustrierte Zeitung für Blechindustrie
Zts. Akklimat.	Zeitschrift für Akklimatisation: Organ des Akklimatisations-Vereins in Berlin
Zts. allg. Erdkunde	Zeitschrift für allgemeine Erdkunde
Zts. allg. österr. Apoth.-Ver.	Zeitschrift des allgemeinen österreichischen Apotheker-Vereins
Zts. allg. Physiol.	Zeitschrift für allgemeine Physiologie
Zts. anal. Chem.	Zeitschrift für analytische Chemie
Zts. Anat.	Zeitschrift für Anatomie und Entwicklungsgeschichte
Zts. ang. Chem.	Zeitschrift für angewandte Chemie, und Zentralblatt für technische Chemie
Zts. ang. Mikr.	Zeitschrift für angewandte Mikroskopie mit besonderer Rücksicht auf die mikroskopischen Untersuchungen von Nahrungs- und Genussmitteln, technischen Produkten, Krankheitsstoffen, etc.
Zts. anorg. Chem.	Zeitschrift für anorganische Chemie
Zts. Bauwesen	Zeitschrift für Bauwesen
Zts. Berg-Hütten Salinenw.	Zeitschrift für das Berg-Hütten und Salinenwesen im Preussischen Staate
Zts. Biol.	Zeitschrift für Biologie

Zts. Bot.	Zeitschrift für Botanik
Zts. Chem.	Zeitschrift für Chemie
Zts. chem. Apparat.	Zeitschrift für chemische Apparatenkunde (Discontinued)
Zts. Chem. Ind.	Zeitschrift für die Chemische Industrie mit besonderer Berücksichtigung der chemisch-technischen Untersuchungsverfahren 1887; later Zts ang Chem.
Zts. chem Ind. Kolloide	Zeitschrift für Chemie und Industrie der Kolloide
Zts. Chemotherap.	Zeitschrift für Chemotherapie und verwandte Gebiete. (formerly Folia Serologia)
Zts. deut. geol Ges Abh.	Zeitschrift der deutschen geologischen Gesellschaft Abhandlungen
Zts. deut. Landw.	Zeitschrift für deutsche Landwirthe
Zts. Dreschler	Zeitschrift für Dreschler, Elfenbeingraveure und Holzbildhauer
Zts. Dungerw.	Zeitschrift für Dungerwesen
Zts. Electrochem.	Zeitschrift für Electrochemie
Zts. Entom. (Breslau)	Zeitschrift für Entomologie im Auftrage des Vereins für schlesische Insektenkunde zu Breslau
Zts Ethnol.	Zeitschrift für Ethnologie
Zts. exper. Path. Therap.	Zeitschrift für experimentelle Pathologie und Therapie, Berlin
Zts. Farben-Ind.	Zeitschrift für Farben-Industrie
Zts. Feuerwehr.	Illustrierte Zeitschrift für die deutsche Feuerwehr
Zts. Fischerei	Zeitschrift für Fischerei
Zts. Fleisch. Milchhyg.	Zeitschrift für Fleisch- und Milchhygiene
Zts. Geburtsh.	Zeitschrift für Geburtshilfe und Frauenkrankheiten
Zts. Geburtsh. Gynakol	Zeitschrift für Geburtshilfe und Gynakologie
Zts. ges Brauw.	Illustrierte Zeitschrift das gesamte Brauwesen
Zts. ges. Getreidew.	Zeitschrift für das gesamte Getreidewesen
Zts. ges. Naturwiss.	Zeitschrift für die Gesamten Naturwissenschaften
Zts. Ges. Ornith.	Zeitschrift für die gesamte Ornithologie
Zts. ges. Textilind.	Zeitschrift für die gesamte Textilindustrie
Zts. ges. Wasserwirts.	Zeitschrift für die gesamte Wasserwirtschaft
Zts. Heilk.	Zeitschrift für Heilkunde, als Fortsetzung der Prager Vierteljahrsschrift für praktische Heilkunde
Zts. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten
Zts. Immunit. Abt. I 13.	Zeitschrift für Immunitätsforschung und experimentelle Therapie. Abteilung I. 13 Abteilung II. or
Abt. Ref.	Ref. 1 vol
Zts. Induk. Abst. Vererbungslehre	Zeitschrift für Induktive Abstammungs- und Vererbungslehre
Zts. Instrumentenk.	Zeitschrift für Instrumentenkunde
Zts. Klin. Med.	Zeitschrift für Klinische Medizin
Zts. Krebsforsch.	Zeitschrift für Krebsforschung
Zts. Kryst. Mineral.	Zeitschrift für Krystallographie und Mineralogie
Zts. landw. Versuchsw.	Zeitschrift für das landwirtschaftliche Versuchswesen in Oesterreich
Zts. Malakozool.	Zeitschrift für Malakozoologie
Zts. Math. Phys	Zeitschrift für Mathematik und Physik
Zts. math. Unterr.	Zeitschrift für mathematischen und naturwissenschaftlichen Unterricht
Zts. Mikro. Tek.	Zeitschrift für Mikroskopischen Technik.
Zts. Morphol. Anthrop.	Zeitschrift für Morphologie und Anthropologie
Zts. Nahr. Genuss. (Z. genuss)	Zeitschrift für Untersuchung der Nahrungs und Genussmittel, sowie der Gebrauchsgegenstände
Zts. Naturwiss.	Zeitschrift für Naturwissenschaften...im Auftrage (Organ) des Naturwissenschaftlichen Vereins für Sachsen und Thüringen

Zts. öffentl. Chem.	Zeitschrift für öffentliche Chemie
Zts. Ohrenheilk.	Zeitschrift für Ohrenheilkunde in deutscher und englischer Sprache
Zts. österr. Ing. Ver.	Zeitschrift des österreichischen Ingenieur und Architekten Vereins
Zts. paraf. Ind.	Zeitschrift für Parafin Industrie
Zts. Parasit.	Zeitschrift für Parasitenkunde
Zts. Pflanzenkrankheiten	Zeitschrift für Pflanzenkrankheiten
Zts. physik. Chem.	Zeitschrift für physikalische Chemie, Stochiometrie und Verwandtschaftslehre
Zts. Physik. Chem. Unterr.	Zeitschrift für dem physikalischen und chemischen Unterricht
Zts. Physiol. Chem.	Zeitschrift für physiologische Chemie (Hoppe-Seylers)
Zts. prakt. Geol.	Zeitschrift für praktische Geologie
Zts. Psychol.	Zeitschrift für Psychologie und Physiologie der Sinnesorgane
Zts. ration. Med.	Zeitschrift für rationelle Medicin
Zts. Reprodukt.	Zeitschrift für Reproduktionstechnik
Zts. Rubenzuckerind.	Neue Zeitschrift für Rubenzuckerindustrie
Zts. Schiess Spreng.	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen
Zts. Spiritusind.	Zeitschrift für Spiritusindustrie
Zts. Telegr. Ver.	Zeitschrift des deutsch-österreichischen Telegraphen-Vereins
Zts. Thiermed.	Zeitschrift für Thiermedizin
Zts. Tuberkulose	Zeitschrift für Tuberkulose und Heilstättenwesen
Zts. Ver. deut. Ingen.	Zeitschrift des Vereins deutscher Ingenieure
Zts. Ver. Rubenzuckerind.	Zeitschrift des Vereins für die Rubenzucker-Industrie des deutschen Reichs
Zts. Ver. Zuckerind.	Zeitschrift des Vereins der deutschen Zuckerindustrie
Zts. Wiss. Geogr.	Zeitschrift für wissenschaftliche Geographie
Zts. wiss. Mikro	Zeitschrift für wissenschaftliche Mikroskopie
Zts. wiss. Photochem	Zeitschrift für wissenschaftliche Photographie, Photo-physik, und Photochemie
Zts. wiss. Zool.	Zeitschrift für wissenschaftliche Zoologie
Zts. Zuckerind.	Zeitschrift für Zuckerindustrie
Zts. Zuckerind. Böhm	Zeitschrift für Zuckerindustrie in Böhmen
Zürich. Denkschr. Med. Chr. Ges.	Denkschrift der medizinisch-chirurgischen Gesellschaft des Kantons Zürich
Zürich. Mitth.	Mittheilungen der Naturforschenden Gesellschaft in Zürich
Zürich, Monats.	Monatsschrift des wissenschaftlichen Vereins in Zürich
Zürich naturf. Ges.	Vierteljahrsschrift der naturforschenden Gesellschaft in Zürich
Zürich Physik. Ges. Jahr.	Jahresbericht der physikalischen Gesellschaft in Zürich
Zürich, Schweiz. Ges. Neue Denkschr.	Neue Denkschriften der allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften
Zürich, Soc. Entom.	Societas Entomologica Organ für den internationalen Entomologenverein. Zürich
Zürich, Unters. Physiol. Lab.	Untersuchungen aus dem Physiologischen Laboratorium der Züricher Hochschule
Zürich, Verh.	Verhandlungen der Medicinisch-chirurgischen Gesellschaft des Kantons Zürich im Jahr 1826
Zürich, Vierteljahrsschr.	Vierteljahrsschrift der Naturforschenden Gesellschaft in Zürich
Zwickau Ver. Naturk. Jahr	Jahresbericht des Vereins für Naturkunde zu Zwickau
Zwolle, Vooruitgang.	De Vooruitgang; Tijdschrift voor Wetenschap



## CHAPTER I

### HISTORICAL DEVELOPMENT of CELLULOSE ETHERS

THE ETHERIFIED derivatives of carbohydrate bodies in general and of the celluloses in particular,—the cellulose ethers both alkyl and aryl,—and in contradistinction to the carbohydrate carboxylates or cellulose esters typified by acetylated cellulose, comprise an art which has had its inception and development entirely in the Twentieth Century, and from the trend of technical development in the past decade only, comprehending the issuance of over fifteen hundred separate patents, in many respects appears to offer greater industrial possibilities and more diversified ramifications than that attained by the better known, more firmly established, and more exhaustively investigated esterified celluloses.

In comparison with the cellulose ethers, the esterified derivatives of cellulose, both the inorganic esters typified by the cellulose nitrates and the organic esters represented by the cellulose acetates, the cellulose esters have been known for a much longer period. The history of the nitrated celluloses goes back to the early thirties of the past century and the initial experiments of Henri Braconnot on xyloidine in 1833<sup>1</sup>; while the development of the organic cellulose esters had its inception in the memoir of Paul Schuetzenberger published in 1865<sup>2</sup> on the action of acetic acid upon cellulose and starch, as detailed in the next Chapter. It was not until forty years later, that W. Suida conceived the idea of substituting alcoholic radicals for hydrogen in the replaceable hydroxyls of cellulose instead of acid radicals, and thus, unwittingly or otherwise, opened up an entirely new and broad field in organic chemistry,—the theoretical investigation and technical exploitation of the etherified celluloses.

1. For details, see E. Worden, "Nitrocellulose Industry," 2 vols., (1911); "Technology of Cellulose Esters," Vol. I, part 3, (1921).

2. For details consult, E. Worden, "Technology of Cellulose Esters," Vol. 8, (1915).

An interesting prelude to the work of Suida on the alkylation of cellulose is found in prior disclosures of alkylating non-cellulosic bodies, primarily in the sugar group. As far back as 1860, M. Berthelot<sup>1</sup> heated cane sugar with ethyl bromide and caustic potash, and obtained a substance which he described as a diethylglucosan ether. E. Fischer<sup>2</sup> prepared alkyl glucosides by the condensation of carbohydrates and an alcohol through the agency of hydrochloric acid, and detailed the preparation and properties of methyl-, ethyl- and benzyl-glucose, methyl- and ethyl-arabioside and methylrhamnoside, the ethylglucoside being identical with the "diglucose" of A. Gautier<sup>3</sup>. Fischer also saturated an alcohol solution of benzoin<sup>4</sup> with gaseous HCl, and obtained methylbenzoin and ethylbenzoin, and in 1895 he prepared various *a*- and *b*-methylglucosides<sup>5</sup>, ethylglucosides, methylgalactosides, methylglucoheptoside, methylxylosides, methylsorboside, methylfructoside and the products of methylation of benzoylcarbinol.

W. Koenig and E. Knorr<sup>6</sup> advanced the subject by the formation of tetracetyl-methylglucosides (*a* and *b*), tetracetyl-*b*-ethylglucoside and *b*-ethylglucoside. T. Purdie and J. Irvine<sup>7</sup> showed that the hydrogen atoms in the alcoholic hydroxyl groups could also be replaced by alkyl rests by the use of silver oxide and alkyl iodide, and prepared trimethyl-*a*-methylglucoside, tetramethyl-*a*-methylglucoside and tetramethylglucose. L. Maquenne<sup>8</sup> described the preparation of *b*-methylglucoside.

**Pioneer Work of Suida.** In 1904-1905 Wilhelm Suida was keenly interested in the tinctorial properties of various dyestuffs in relation to carbohydrate bodies, from the viewpoint principally of the elucidation of the structure

1. Ann. Chim. Phys. 1860, **60**, 103.
2. Ber. 1893, **26**, 2400; abst. J. C. S. 1894, **66**, i, 3.
3. Bull. Soc. Chim. 1874, (2), **22**, 145.
4. Ber. 1893, **26**, 2412; abst. J. C. S. 1894, **66**, i, 38.
5. Ber. 1895, **28**, 1145; abst. J. C. S. 1895, **68**, i, 437.
6. Ber. 1901, **34**, 957; abst. J. C. S. 1901, **80**, 369.
7. J. C. S. 1903, **83**, 1021.
8. Bull. Soc. Chim. 1905, **33**, 469.



of carbohydrates in general and cellulose in particular, by the effect of various coloring materials thereon. In 1904 there was published a resume of his investigations upon the avidity and tenacity with which certain named dyestuffs adhere to or combine with the starches, especially potato starch<sup>1</sup>.

On January 12th, 1905, the Monatshefte fuer Chemie of Vienna received for publication, a memoir that probably embraces the first coherent description of the etherified celluloses, being an examination into the effect of the atomic groups of cellulose and textile fibers, and their influence upon the dyeing process<sup>2</sup>. After reviewing the work of his predecessors in this field<sup>3</sup>, he described methods for the preparation of methylcellulose and ethylcellulose—but in a rather fragmentary manner.

That portion of this premier communication on the cellulose ethers of pertinence in this connection is as follows:

“Basing our assumption on the premises that cellulose possesses the nature of an anhydride alcohol, the active groups can then only consist of alcoholic hydroxyls. It appeared not impossible that the comparatively large number of these hydroxyls, and the presence of oxygen atoms of varied linkage in the cellulose molecule, would endow some

1. Monats. 1904, **25**, 1107; abst. J. C. S. 1905, **88**, i, 75; Meyer Jahr. Chem. 1905, **15**, 512; Wagn. Jahr. Chem. 1905, **51**, 479; Chem. Centr. 1905, **76**, 128; Chem. Zts. 1905, **4**, 224.

2. Monats. 1905, **26**, 413; abst. J. C. S. 1905, **88**, 457; Meyer Jahr. Chem. 1905, **15**, 512; Chem. Zts. 1905, **4**, 444; J. S. C. I. 1905, **24**, 543; Chem. Centr. 1905, **76**, i, 1348. Sitzber. d. Akad. d. Wissensch. Wien, Math. nat. Kl. 114, Jan. 1905; abst. Wagn. Jahr. Chem. 1905, **52**, 480. Wien. Akad. Ber. **114**, IIb, 43; abst. Jahr. Chem. 1905-08, II, 3158. Sitzungsber. d. Kaiserl. Akad. Wissensch. Wien, Math. nat. Kl. 64, IIb, Jan. 1905; abst. Lehne Faerberztg. 1905, **1**, 105, 140.

3. F. Kuhlmann, Compt. rend. 1856, **42**, 673, 711; **43**, 900, 950. L. Vignon, Compt. rend. 1890, **110**, 286, 909; 1891, **112**, 487, 580, 623. C. Weber, Dingl. poly. J. 1892, **283**, 158, 183; **289**, 160, 186. E. Reisse, Lehne's Faerberztg. 1894-1895, 330, 351. E. Knecht, Ber. 1889, **22**, 1120. P. Richard, Chem. Ztg. 1888, **12**, 1378. F. Schoen, Lehne's Faerberztg. 1892-1893, 152. R. Wolfenstein and G. Bumcke, Ber. 1899, **32**, 2493; 1901, **34**, 2415. A. Binz and G. Schroeter, Ber. 1903, **36**, 3014.

of these hydroxyl radicals with acidic properties, especially as it is known that alkali compounds of cellulose exist, although probably accompanied by partial hydrolysis and hydrocellulose formation. In that way cellulose may resemble the saccharates.

"If now, these hydroxyl radicals were active groups in the sense I assumed them to be, they could be rendered relatively inactive by means of acylation or alkylation. The nitrocelluloses are assumed to be acylated hydrocelluloses. In the literature there have been described a tri- and a penta-acetylcellulose (according to A. Wagner, D. R. P. 152432, cellulose acetate filaments do not absorb dyes); but these are amorphous, and although I have taken the trouble to prepare them, they do not come within the scope of this article.

"Attempts to acylate cellulose by treating the same with *acetyl* chloride, or *benzoyl* chloride<sup>1</sup> on a waterbath, alone, or with *sodium* hydroxide or *pyridine*, lead to products of unchanged structure which had taken up as much as one acid molecule per molecule of cellulose (based on a  $C_6$  formula), which was determined by saponification with alcoholic potash and titrating back. However, it seemed that even then considerable hydrolysis had taken place, hydrocellulose being formed, as the fibers appeared to be much weakened.

"Attempts to alkylate cellulose in the presence of acids led to still poorer results. The fibers disappeared every time after a short period. Partially acylated and benzoylated cotton, as well as *alkylated cotton* prepared from *alcohol* and sulfuric acid, and that obtained by treatment with *dimethylsulfate* and alkalies, and nitrocellulose containing 12.1% N, all behave exactly the same when dyeing tests were made in comparison with untreated cotton, fuchsine, crystal violet, Bordeaux and azofuchsine being the

1. It will be remembered that the action of benzoyl chloride upon cellulose results in the formation of an ester (cellulose benzoate), while the action of benzyl chloride upon cellulose forms a cellulose ether (benzylcellulose).

dyes used. The dyeings obtained with the first three dyestuffs were exactly alike, while the azofuchsine failed to dye any of the fibers.

“(Note:—In contradistinction to Kuhlmann I found that, under the conditions of my experiments, that guncotton behaves no different to dyestuffs than does ordinary cotton.) . . .

“Dyeings were made on ordinary and on benzoylated cotton, and were examined microscopically by Dr. Ritter von Hoehnel, but absolutely no difference could be detected between the benzoylated and the ordinary cellulose . . . . Thus it can be assumed that the dyeing process depends rather on a dissociation of the dye molecule brought about by the cellulose . . .

“How energetically cotton may act as a catalyst was shown by an attempt to benzoylate the same according to the method of Schotten-Baumann. Equal parts of benzoyl chloride and sodium hydroxide were placed in flasks. To one sample, some well moistened cotton was added. Both samples were then well shaken. In the sample containing the cotton, the benzoyl chloride disappeared at once, and after a few minutes the cotton appeared to swell up, the liquid became turbid and in fifteen minutes the whole mass had changed to a soft paste. Examination of this showed that it consisted of unchanged cotton, sodium chloride and benzoic acid. The duplicate sample without the cotton had undergone practically no change. It consisted essentially of benzoyl chloride and sodium hydroxide.

“I assume that the action of the cotton on the dyestuffs follows analogous lines.”

This communication of Suida to the Monatshefte appears to be an entirely academic contribution, and nothing contained therein would indicate that the author was aware of any technical applications that might arise out of his disclosures.

The next year (1906) W. Dreaper published his work on "Chemistry and Physics of Dyeing," on page 20 of which appears the paragraph:

"If the cellulose aggregate or molecule is an alcoholic anhydride, its chemical activity might be due to its hydroxyl groups. Various acyl and alkyl derivatives have been prepared and their relative dyeing properties determined by W. Suida (*Monatsh. f. Chem.* 1905, **26**, 413). The results show that the dyeing properties of the nucleus are not influenced by the conversion of these OH groups into the acyl or alkyl ones. These results should be considered in conjunction with nitrocellulose and hydrocellulose."

From an examination of the work of Dreaper in its entirety, there is no observable indication that he was aware of the future possible technical significance of the primary disclosure of Suida in this rapidly expanding field.

There is a question as to whether the compounds described by A. Nastukoff in 1902<sup>1</sup> and further amplified in 1907<sup>2</sup>, can properly be characterized as an etherized cellulose. He described a compound obtained by the action of benzene upon a strong sulfuric acid solution of cellulose, which first was considered as a tetraphenylcellulose, but subsequently found to contain small amounts of chemically combined sulfur. The product, when dried at the ordinary temperature in a desiccator, corresponds to a tetraphenylcellulose, plus 2 molecules SO<sub>2</sub>, and from which a corre-

1. J. Russ. Phys. Chem. Soc., 1902, **34**, 231, 505; abst., J. C. S., 1902, **82**, i, 362, 747; Chem. Centr., 1902, **73**, I, 1277; II, 576; Chem. News, 1903, **88**, 255; J. S. C. I., 1902, **21**, 1302; Zts. Farben u. Textchem., **1**, 633; abst., Chem. Centr., 1903, **74**, I, 139.

2. J. Russ. Phys. Chem. Soc., 1907, **39**, 1109; Zts. Farb. Ind., 1907, **6**, 701; abst. Chem. Zentr., 1907, **78**, I, 820; J. C. S., 1907, **92**, i, 413; J. S. C. I., 1907, **26**, 282; C. A., 1908, **2**, 1274; Jahr. Chem. 1905-08, II, 1427; Zts. ang. Chem., 1907, **20**, 1782. Compare E. P. 28638, 1902; abst., J. C. S. I., 1903, **32**, 414; Chem. Ztg., 1904, **28**, 435. F. Ephraim, Ber., 1901, **34**, 2780; abst., J. C. S., 1901, **80**, i, 688; Bull. Soc. Chim., 1902, **28**, 150; Chem. Centr., 1901, **72**, II, 1008; Jahr. Chem., 1901, **54**, 1271. For glucose phenyldeoxine, see A. Nastukoff and J. Kotjukow, Bull. Soc. Chim., 1909, (4), **6**, 579; 1913, (4), **13**, 102; Jour. Russ. Phys. Chem. Soc., 1912, **44**, 1152; abst. Chem. Zentr., 1913, I, 19. F. Fischer and W. Schneider, J. S. C. I., 1920, **39**, 225-A.

sponding nitrate and sulfonate can be obtained. Upon dry distillation of this compound, toluene is obtained as the main product, while 45% benzoic acid is yielded upon oxidation with potassium or sodium permanganate.

By varying the method of treatment of cellulose in sulfuric acid with benzene, the product has been prepared containing as small amount of sulfur as 0.43%, and this product has been named *b*-phenyldesoxyn to distinguish it from the former material, to which the name phenyldesoxyn was given. The product appears to be derived from cellulose by the replacement of three hydrogen by three phenyl groups, and if this is so, may be properly classified as an etherified cellulose—triphenylcellulose.

On oxidation with permanganate or bichromate, the desoxyns yield monobasic or polybasic acids corresponding to the hydrocarbons employed, together with carbon dioxide and oxalic acid. For instance, benzoic acid is obtained from phenyldesoxyn, terephthalic acid from tolyldesoxyn, terephthalic and trimellitic acids from pseudocumyldesoxyn. The composition of phenyldesoxyn when prepared containing a minimum of sulfur, and neglecting this sulfur, corresponds fairly well with the formula  $C_6H_7O_2(C_6H_5)_3$ , that is, cellulose in which the three hydroxyls are replaced by phenyl groups<sup>1</sup>, and the properties of the desoxyns correspond in many respects with this view of their constitution. Analogous products are obtained if dextrose is used instead of cellulose.

Leuchs, Lilienfeld and Dreyfus. The primary disclosures of Suida apparently attracted little attention, the subject remaining quiescent for over seven years, and by a peculiar coincidence was awakened from its dormancy in 1912 by the filing in Germany, Austria and France by chem-

1. A. Green, Zts. Farben u. Textil Chem., 1904, **3**, 97; abst. J. S. C. I., 1904, **23**, 382.

These three basic patents are reproduced herewith in extenso in condensed form, because they form the basis for future technical development, and have instigated extensive litigation which, as yet, has not been adjudicated.

ists of the three countries working independently, patent applications covering the practical production of cellulose ethers.

In that year Otto Leuchs filed his German application on January 12th, which smoldered in the Patent Office archives for over seven years, and then issued under the name of Farbenfabriken vorm. F. Bayer & Co., on July 1st, 1920. Leon Lilienfeld filed his first application in Austria on March 16th, 1912, and Henry Dreyfus in France on the November 18th following.

These three basic patents, forming as they do the primary patent disclosures in this art, are reproduced herewith in condensed form, as they have formed in a large measure the basis for future technical development, and have instigated extensive litigation which, as yet, has not been adjudicated.

**Patented Process of Leuchs.** There was received in the German Patent Office on January 12, 1912, the first application for patent protection for a cellulose ether composition<sup>1</sup>, applied for by Otto Leuchs. According to the patentee the subject of the invention is a process for the manufacture of cellulose compounds which, from the manner of their preparation, are probably to be conceived as ethers of cellulose. The process depends upon the action of alkyl halogens on the cellulose derivatives by means of alkalis or alkaline agents.

The cellulose ethers obtained are formed as colloids. They are insoluble in water, caustic alkalis and dilute acids; dissolve in most organic solvents, as alcohol, ether, chloroform, benzene, benzine, carbon tetrachloride, ethyl acetate and acetone. According to the method of preparation, many

1. D. R. P. 322586. Although this invention was applied for in 1912, it quiesced in the German Patent Office archives until 1920, when it issued on July 1 under the name of Farbenfabriken vorm. F. Bayer & Co. Abstracted Chem. Zentr. 1920, IV, 416. See remarks by Wedorf on the authorship of this invention, Kunst. 1920, 10, 113; abst. Chem. Zentr. 1920, IV, 753; Caout. Guttap. 1922, 19, 11379. O. Leuchs, Kunst. 1920, 10, 145.

products dissolve only partially in one of the solvents, e.g., benzene, whereas the rest only swell up and must first be dissolved in another solvent, as alcohol. This variable solubility leads to the conclusion that various ethers are formed together, which can also be expected theoretically to fall into three groups, namely, mono-, di- and tri-derivatives.

From their solutions, as in benzene, the ethers as a rule dry like collodion solutions. There remains behind clear, transparent skins which can be used as films. They do not ignite when exposed to heat, nor do they melt. The products may also be utilized for the production of artificial silk, and in combination with camphor and camphor substitutes, for the preparation of masses of the nature of celluloid. The solutions may also be used for the production of waterproof lacquers.

As starting material, cellulose in every form, wadding, filter paper, pulp, etc., may be used. As alkalis and alkaline substances, there come into consideration sodium or potassium hydroxide, ammonium hydroxide, alkaline earths, sodium zincate or aluminate, also metallic oxides as copper oxide, which is taken up by alkaline solutions of cellulose (Normann's copper-alkali-cellulose). The alkylating agent may be used in solution, diluted with benzene. Several alkylating agents may be used simultaneously for the preparation of mixed ethers.

As an example, cellulose is allowed to soak in a strong solution of sodium hydroxide (e.g. 1:1) for 1-2 days or longer, the excess lye being then removed by pressing or centrifugalizing, and the cellulose dried if necessary, either in vacuo or by distillation with benzene or petroleum, to a low water content. The sodium cellulose thus obtained is heated under pressure with 3 parts ethyl chloride calculated on one part of cellulose used, perhaps with stirring in a closed vessel, at about 130° for 8 hours. An excess of ethyl chloride does not matter. The length of heating depends on the temperature, at lower temperatures a longer period of heating being required.

For isolation of the ethers formed, the excess of ethyl chloride is distilled off, the residue extracted with water for the removal of salts, and after drying is dissolved as by alcohol, filtered under pressure, and the ethylcellulose precipitated therefrom by dilution with water. It is obtained as a white, amorphous powder. One proceeds in an analogous manner with other halogen alkyls. As a rule, two molecules of alkylating agent are used per molecule of cellulose.

The ratio between cellulose, alkali and alkyl-halogen is to be so proportioned that the side reactions which appear more or less in the process, such as the splitting off of halogen halides and alkyl-halogen, and the formation of acids and alkali-consuming materials from the cellulose, do not hinder the course of the reaction on account of a deficiency of alkali and alkyl chloride.

There was filed in the U. S. Patent Office on August 8, 1917, an application by O. Leuchs<sup>1</sup>, which, on account of hostilities, apparently never eventuated into patent acceptance. It had to do with the composition of a varnish of ethyl-, propyl- or benzyl-cellulose dissolved in benzene or in a solvent comprising or containing benzene. A method of benzylcellulose manufacture was disclosed, comprising mixing 40 gms cellulose with 400 gms 10% caustic soda, then 800 gms caustic soda are added, after which the mixture is heated with 500 gms benzyl chloride for 50-70 hours at 100°. The mass obtained is washed with ether-alcohol and finally with water, and when dried is a pure white powder, soluble in benzene, or a mixture of benzene with alcohol and chloroform.

**The Original Lilienfeld Process for Cellulose Ether Manufacture.** As previously stated, the first of the original Lilienfeld patents to be published bears the British

1. Serial No. 185198, filed Aug. 8, 1917; official letter Aug. 28, 1917; Lilienfeld, E. P. 12854, 1912 and 6035, 1913 cited against applicant. Nine claims. The invention was assigned to Farbenfabriken vorm. F. Bayer & Co., and came into the possession of Synthetic Patents Co.



number 12,854 of 1912, the application date being May 31, 1912, the complete specification left December 31, 1912, and the patent accepted September 1st of the year following.

The object of the invention is to formulate a process for the production of cellulose ethers, i.e., compounds of cellulose and its conversion products with alcohols, in which one or more hydroxyl hydrogens of cellulose are replaced by alcohol radicals<sup>1</sup>. This group of bodies comprises a large number of members differing from one another in their properties according to the nature and number of alcohol radicals that are linked ether-fashion with the cellulose molecule, all having in common a high degree of stability and neutrality, which, when combined with a greatly diversified range of solubilities and valuable physical properties, render these ethers suitable for a wide variety of uses.

This replacement of hydroxyl hydrogens of cellulose by alcohol radicals may be effected by causing esters of inorganic acids to act upon cellulosic products in the presence of basic substances free or combined with the cellulose.

1. U. S. P. 1188376, 1916; applied for June 26, 1912; abst. C. A. 1916, **10**, 2145; J. S. C. I. 1916, **35**, 887; Mon. Sci. 1917, **84**, 28; Chem. Ztg., 1916, **14**, 805; Kunstoffe, 1916, **6**, 282. E. P. 6035, 1913, date applied for March 16, 1912, claimed from the date of first foreign application; abst. C. A. 1914, **8**, 2947; J. S. C. I. 1914, **33**, 417; Chem. Ztg. 1913, **37**, 472; 1914, **38**, 419; Chem. Ztg. Rept. 1914, **38**, 490; Kunstoffe, 1914, **4**, 435. E. P. 12854, 1912; applied for May 31, 1912; abst. C. A. 1913, **7**, 3839; J. S. C. I. 1913, **32**, 940; Chem. Ztg. 1913, **37**, 1205; 1914, **38**, 419; Chem. Ztg. Rept. 1914, **38**, 490. F. P. 447974, applied for July 17, 1912; claims Austrian application dated March 16, 1912; abst. J. S. C. I. 1913, **32**, 420; Mon. Sci. 1914, **80**, 3; Chem. Ztg., 1913, **37**, 122; Kunst. 1913, **3**, 195. Belg. P. 254591; abst. Chem. Ztg. 1913, **37**, 567; Kunst. 1913, **3**, 355. F. P. 459972; abst. J. S. C. I. 1913, **32**, 1153. Hung. P. L-3451; abst. Chem. Ztg. 1919, **43**, 753. Ital. P. 132825; abst. Chem. Ztg. 1913, **37**, 1334. Aust. 63526; abst. J. C. S. 1914, **106**, i, 919. Aust. P. 73001; abst. Kunstoffe, 1917, **7**, 222; Meyers Jahr. Chem. 1918, **28**, 219; Aust. P. 78217. Span. P. 55104; abst. Chem. Ztg. 1913, **37**, 728. Swiss P. 66512; abst. Chem. Ztg. 1914, **38**, 1034; Kunstoffe, 1915, **5**, 70. Norw. P. 27507; abst. C. A. 1917, **11**, 1748. D. R. P. 477154; abst. C. A. 1929, **23**, 4071. D. R. P. 470142; abst. Chem. Zentr. 1929, I, 1528. Dan. P. 18285. Swed. P. 38905. Ital. P. 140506.

The following raw or primary materials may be employed:

1. Bleached or unbleached cellulose in any form.
2. Substances containing cellulose, as wood, wood pulp, cotton, flax, hemp, jute, esparto, rice husks, vegetable pith.
3. Conversion products allied to cellulose, as hydrolyzed or oxidized cellulose (cellulose hydrate, hydracellulose, acid-cellulose, sulfohydrocellulose, colloidal cellulose, celloxin), which are obtained by treating cellulose with peroxide, perborate, persulfate, percarbonate, permanganate, chromic acid, bichromate, nitric acid, calcium hypochlorite, hypochlorites or hypobromites, chlorates in acid solution, chlorine or bromine alone or in the presence of inorganic or organic acids, sulfur chloride, oxygen, ozone, ammonium cupric oxide, zinc chloride and other zinc halides, organic and inorganic acids in the cold or in the heat, alkalis cold or hot.

To this class belong the cellulose derivatives soluble in aqueous alkalis which are very suitable for the present process, in the form in which they are obtained by treating cellulose with hot alkaline liquors, with ammonium cupric oxide and subsequent precipitation, with zinc halides alone or in conjunction with 45-60° Be. sulfuric acid, and subsequent water precipitation. There also may be used the alkali-soluble cellulose conversion products produced by the action of saponifying agents upon their esters (cellulose nitrates, acetates, formates), and those obtained by treating raw or refined cellulose xanthates (viscose) with acids, metallic salts, heat or spontaneous coagulation.

Artificial silk and artificial silk waste may be used in the process.

A. All inorganic and organic simple and mixed cellulose esters (nitrocellulose, acetylcellulose, formylcellulose, lactylcellulose, cellulose phosphate, formycellulose phosphate). If basic substances are present in the reaction mixture, usually a saponification of the esters will take

place. The resulting salts of the acid components have no pronounced unfavorable influence on the reaction. Therefore, the cellulose or cellulose hydrate which is liberated at the same time reacts exactly in the same manner, and produces the same ethers as cellulose hydrate. In event of incomplete saponification of the esters, the product will be a cellulose ether containing ester groups.

The process may be carried out by treating cellulosic materials in the presence of esters of inorganic salts and of basic substances, haloid esters (halogen-substituted alcohols), and sulfuric acid esters being examples. If the alkali-compounds of cellulose (mercerized cellulose), cellulose hydrate, oxycellulose, cellulose xanthogenate, or compounds of these bodies with alkaline earths, ammonium, zinc, silver or lead be employed as primary materials, then "the basic substances are fixed to the cellulose bodies." In other cases, the basic catalytic or dehydrating substances are contained in a free state in the reaction mass. The process may also be carried out by adding to the reaction mixtures a further quantity of basic substances as alkali, alkali metals, alkali alcoholates, in addition to the basic substances fixed to the cellulose bodies. The desired amount of basic substances may be added to the reaction mixture all at once at the beginning, or gradually during the reaction, either undissolved, or dissolved in various solvents, as likewise may be the cellulosic materials.

For instance, if the primary materials employed are the cellulose hydrates, oxycellulose, cellulose xanthate or colloidal cellulose or their metallic derivatives which are water-soluble or dissolve in aqueous alkalis, ammonia or the like, the reaction may be carried on either in an aqueous or alcoholic solution. Or the operation may be initiated with an aqueous-alkaline solution, and an alcoholic solvent or diluent, as an alcohol, hydrocarbon or pyridine added during the reaction, either in one or several portions.

These solvents or diluents may also be employed for dissolving the basic substances (i.e., alkali hydroxide, alkali

metal, alkali alcoholate, ammonia or pyridine). When the primary materials employed are cellulose esters soluble in organic solvents, they may be brought into the reaction by solution in alcohol or pyridine. The process may be initiated with undissolved celluloses as cellulose or alkalicellulose. In all cases, when operating with dissolved or undissolved cellulosic substances, the reaction may be carried out in the presence or absence of cellulose ether solvents (alcohol, benzene, pyridine). When basic substances as pyridine are used, they act both as solvent and basic substances. The esters of inorganic acids may be added at once or gradually. The reaction may take place either at ordinary pressure or in a vacuum or under pressure, air being excluded if desired, by the use of neutral gases, or in the presence of catalysts, condensing or dehydrating agents.

In most cases the ethers may preferably be separated out from aqueous reaction mixtures by bringing the hot reaction mass, either after neutralization or acidification in any convenient manner, then washed thoroughly with hot water until neutral. If the cellulose ethers are in the dissolved state in the reaction mixture, as would ensue where the etherification takes place in the presence of a solvent, they may be precipitated by the addition of water or salts solution. Or, they may be removed by the use of a liquid in which the cellulose ethers are soluble and the reaction by-products insoluble. They may be purified by re-solution and re-precipitation in a large bulk of water.

Inasmuch as cellulose contains several alcoholic hydroxy hydrogens, this process allows of varying the number of hydroxyl hydrogens replaceable by alcohol radicals. The number of radicals introduced depends on the quantity of inorganic ester used, and also on the working conditions of temperature, nature and quantity of basic substances employed and reaction mixture concentration or, by preparing ethers with a lower number of alcohol radicals, and then further etherifying. The free hydroxyl groups of the cellulose ethers in which not all the hydroxyl hydrogens have

been replaced by alcohol radicals, have a tendency to form compounds with basic substances, and especially alkali metals or their hydroxides, as is shown by the fact that many alcohol-soluble cellulose ethers not of maximum etherification, yield precipitates when their alcoholic solution is treated with a solution of an alkali. This is due to the fact that, although the free cellulose ethers are soluble in alcohol, their compounds with alkalis are insoluble. For this reason, with such cellulose ethers, it is advisable to liberate the OH group, by treating them with acids or acid salts, which may be done either by adding substances having an acid reaction to the reaction mixture after the completion of etherification, or by separating out the ethers with basic substances, then treating with acids or acid salts.

In many cases it appears that instead of homogeneous cellulose ethers, mixtures are formed which differ from one another by the number of OH-hydrogens replaced by alcohol radicals. Mixed cellulose ethers are obtainable by allowing two or more differing inorganic esters to etherify cellulose. Such mixed ethers may also be produced with one or more introduced uniform alcohol radicals, then treating them with inorganic acid esters containing different alcohol radicals.

The "new" cellulose ethers possess a great variety of properties according to the number and nature of alcohol radicals introduced therein. Many are soluble in water; others insoluble in water but soluble in a number of other solvents. The water-soluble cellulose ethers have the characteristic feature that although soluble in cold water, they are insoluble or difficultly soluble in hot water, and dissolve in a number of other solvents. Their aqueous solutions become precipitated or coagulated by heat. They all have in common a high degree of stability, neutrality and indifference. They withstand being heated to high temperatures with or without water, and also are very stable to hot acids and alkalis. They possess a greater stability than all simple and mixed cellulose esters, and all hitherto described conversion products and derivatives of cellulose. All cellu-

lose ethers have further in common, suppleness, flexibility, power of resistance to chemical and physical influences, remarkable hardness, strength and toughness in films, coatings, filaments and plastics. These advantages are accompanied by the property possessed by many cellulose ethers, of being readily soluble in an almost unlimited number of solvents, and by their slight incombustibility.

Owing to the numerous solvents, the cellulose ethers may be combined with a much larger number of softening and gelatinizing agents, and provides the possibility of combining the ethers with other colloids, plastics and binders.

The following are twelve examples of carrying the Lilienfeld invention into effect:

1. (a) 3750 parts by weight of raw viscose containing about 500 of cellulose and 130-200 of NaOH are diluted with 3750 parts water, and heated with stirring on the water bath until complete coagulation ensues. The coagulated mass which has crumpled into small lumps by the stirring, is thoroughly washed, pressed to 5000 parts, then dissolved in 1000 parts 50% caustic soda solution, the solution being then clarified by filtration.

(b) Cellulose hydrate is precipitated by dilute sulfuric acid from a solution of cellulose in Schweitzer's reagent, and dissolved in caustic soda solution so that 120 parts contain 10 of cellulose hydrate and 10 of sodium hydroxide.

(c) Cellulose is heated with 30-50% NaOH, the liquid poured off, and the resulting cellulose hydrate dissolved in water, precipitated by dilute sulfuric or acetic acids, the precipitated cellulose hydrate after washing, being dissolved as in (b).

1200 (parts by weight) of solution (a), (b), or (c) containing cellulose or cellulose hydrate 100 and caustic soda 100, are mixed with 100-400 of 30% NaOH solution, well stirred and gently warmed. To this are then added

200 of ethyl sulfate in small portions, and the mixture again heated. The turbid reaction mass is diluted with water, acidulated with dilute sulfuric acid, and the resulting ether precipitated and washed to neutrality. The ether may be purified by dissolving in cold water and precipitation by alcohol, heating alone or in presence of saline solutions. The resulting cellulose ethyl ether is a white, pulverulent or flaky substance, readily soluble in cold water, formic acid, cold or hot aqueous acetic acid and aqueous pyridine, but insoluble in alcohol or hot water.

2. 1200 of one of the primary solutions is Ex. 1, containing 100 each cellulose (or cellulose hydrate) and caustic soda, are heated with 100-400 of 30% aqueous NaOH, and mixed gradually with 300 of ethyl sulfate. The reaction mixture is acidified by agitating with dilute sulfuric acid, and washed. The further treatment is as in Ex. 1. The product is white and flaky, readily soluble in cold water, glacial acetic acid, formic acid, pyridine, dichlorhydrin, ethyl formate and aqueous acetone, insoluble in hot water.

3. 1200 of one of the primary solutions as in Ex. 1 is heated on a water bath with 200-400 of 30-40% NaOH solution, then 500 of ethyl sulfate gradually added, the reaction temperature rising with separation of cellulose ether, which is filtered and washed until neutral. The final preparation of the ether is as in Ex. 1. Since this ether is soluble in alcohol, it may be purified by dissolving in alcohol and precipitating by ether or benzene. This ether is readily soluble in cold water, alcohol, methyl alcohol, glacial acetic acid, formic acid, pyridine, dichlorhydrin, nitrobenzene, ethyl formate and aqueous acetone, insoluble in hot water.

4. 1200 of primary solution as in Ex. 1 containing 100 parts each cellulose and caustic soda, are mixed with 500 of ethyl sulfate, heated and gradually mixed with 200 of 30% NaOH, or with the equivalent quantity of 25% alcoholic KOH. The mixture may then be heated. The treatment may consist in immediately diluting with hot water, filtering

and washing the ethyl ether, then subjecting to subsequent treatment with an acid, or acidifying the reaction mixture at the close of the reaction with dilute mineral acid, filtering and washing. Final preparation as in Ex. 3. The finished product is soluble in cold water, alcohol, methyl alcohol, glacial acetic acid, formic acid, pyridine, dichlorhydrin, nitrobenzene, ethyl formate, and aqueous acetone, but insoluble in hot water.

5. 1200 of primary solution as of Ex. 1 containing 100 parts each cellulose and caustic soda, are mixed with 500 of ethyl sulfate, heated on a water bath, and gradually mixed with 130-220 of 50% NaOH, or equivalent quantity of a strong alcoholic caustic potash solution. The mass is then heated, and further treatment as in Ex. 3 and 4. The ether formed is readily soluble in cold water, alcohol, methyl alcohol, formic and glacial acetic acids, pyridine, dichlorhydrin, nitrobenzene, ethyl formate and acetone; gelatinizes in tetrachlorethane, and is insoluble in hot water.

6. 1200 of a primary solution of Ex. 1, containing 100 parts each cellulose and caustic soda, are mixed with 110 of 30% NaOH solution, then 166.6 ethyl sulfate added. After about a half hour another 110 of 30% NaOH and 166.6 ethyl sulfate again added, and the same additions made after the lapse of another half hour, making a total addition of 330 of 30% NaOH and 500 of ethyl sulfate. The separation of ethylcellulose is accompanied by rise in temperature and frothing of the mass. The reaction mixture is diluted with water, and either immediately acidified with dilute sulfuric acid or placed in the alkaline state in a filter and thoroughly washed. In the second case it is preferred to effect a subsequent treatment with an acid or acid salt and again wash. The resulting ethyl ether is insoluble in water, and may be purified by dissolving in alcohol or filtering, or precipitating by water or saline solution and washing. The dry cellulose ether is a white powder, insoluble in hot or cold water, soluble in alcohol, methyl alcohol, formic or glacial acetic



acids, pyridine, dichlorhydrin, nitrobenzene, aqueous acetone or tetrachlorethane.

7. 1200 of one of the primary solutions in Ex. 1 are mixed with 100 of 30% NaOH solution and gently heated, then 100-200 of ethyl sulfate added. The addition takes from  $\frac{1}{2}$ -2 hours. The reaction mixture is then rubbed up with 300-600 powdered NaOH or equivalent amount of KOH. Then the mass is again heated and into it are introduced 300-1300 parts ethyl sulfate gradually at intervals, whereupon the ethylcellulose separates accompanied by rise in temperature and frothing.

After dilution with water, the reaction mass is either immediately acidified with dilute sulfuric acid, or placed in the alkaline condition upon a filter and washed. In the second stage it is preferred to effect a subsequent treatment with an acid or acid salt followed by washing.

The resulting ethylcellulose is a white powder, insoluble in hot or cold water, but readily soluble in the following: methyl or ethyl alcohol, formic or glacial acetic acid, pyridine, quinoline, picoline, dichlorhydrin, epichlorhydrin, nitrobenzene, methyl acetate, ethyl acetate, ethyl phthalate, ethyl sebacate, ethyl tartrate, ethyl citrate, amyl acetate, butyl acetate, ethyl benzoate, ethyl levulinate, acetone, pentachlorethane, tetrachlorethane, ethylene trichloride, acetylene dichloride, carbon tetrachloride, chloroform, benzene, toluene, xylene, phenol, nitrophenols, *o*-cresol, naphthalene, toluidine, aniline, formanilid, acetanilid, turpentine oil, camphor, castor oil, linseed oil, Chinese wood oil, olive oil, vaseline oil, paraffin oil, naphtha (petroleum), vaseline, stearine, beeswax, japan wax, lanolin, nitromethane, phenyl ether, triphenyl phosphate, tricresyl phosphate. Also readily soluble in a mixture of ethyl alcohol and ether, less so in ethyl ether. It can withstand being heated for days with 25% aqueous NaOH solution and also with 25% aqueous caustic potash solution without undergoing decomposition,

and heated for days with water at 170° C. without apparent alteration.

The combustion of a purified sample, dried to uniform weight at 105°, gave the following:

(a) 0.197 gms of sample calculated as ash free gave 0.1562 gms H<sub>2</sub>O, or 8.80% H; 0.4094 gms CO<sub>2</sub> or 56.67% C.

(b) 0.2134 gms sample (ash deducted) gave 0.1719 gms H<sub>2</sub>O, or 8.95% H, and 0.4422 gms CO<sub>2</sub>, or 56.51% C.

Calculated for  $n\text{C}_{22}\text{H}_{40}\text{O}_{10} = n\cdot\text{C}_{12}\text{H}_{15}\text{O}_{10}\cdot(\text{C}_2\text{H}_5)_5$ , 56.89% C and 8.62% H.

9. 1200 of one of the primary solutions of Ex. 1 are mixed with 520-800 of 30% NaOH solution and 1000 ethyl iodide, and digested for some hours at 100°. The result is a somewhat viscid liquid in which is suspended a precipitate partly in the form of flakes and partly as films. The precipitate is collected, washed with hot water, then rubbed up with 100% sulfuric acid and again washed. Purified by solution in alcohol and reprecipitation by water or saline solution. The ethylcellulose is insoluble in hot or cold water, readily soluble in alcohol, methyl alcohol, dichlorhydrin, formic acid, glacial acetic acid, nitrobenzene, aqueous acetone, tetrachlorethane.

10. 1200 parts of one of the primary solutions of Ex. 1 are heated with 520-600 of 30% NaOH solution with a reflux condensing, then 1000 of ethyl iodide added. After protracted heating, the ethylcellulose separates, the product being identical with that of Ex. 9. Working with other ethyl halides, e.g., ethyl bromide and ethyl chloride is similar, their low boiling points however, to be taken into consideration.

11. 750 of soda cellulose (prepared by impregnating cellulose with strong caustic soda solution, squeezing, then triturating) containing 250 cellulose and 250 NaOH, are rubbed up with 310 of 10% NaOH solution and mixed and heated with 1000-2500 of ethyl sulfate. After completion of reaction which occurs with frothing, the cellulose ether

is placed on a filter and washed. A white powder, soluble in cold water, alcohol, methyl alcohol, glacial acetic acid, formic acid, pyridine, nitrobenzene, and aqueous acetone; gelatinizes in tetrachlorethane and is insoluble in hot water. Cellulose ethyl ethers soluble in volatile solvents and insoluble in cold water may be produced from alkalicellulose by varying conditions of working.

12. 1200 of one of the primary solutions in Ex. 1 are mixed with 100 of 30% NaOH solution and gently heated, then 200 of ethyl sulfate gradually added. The mixture is rubbed up with 300-600 of powdered caustic soda, the reaction mixture is again heated on a water bath and to it added 200 potassium ethyl sulfate or equivalent quantity sodium ethyl sulfate in small portions at a time. Further treatment as in foregoing examples.

When carrying out the reactions described in the examples, temperatures between 50-130° are realized, the temperature depending to some extent upon the nature of the ester of the inorganic acid employed, upon the rate at which the ester is made, upon the quantity of material treated, on the concentration of the solution of the initial material, and on the content of basic substance in the reaction mass. By rapidly adding large proportions of inorganic acid esters as ethyl sulfate to a concentrated solution of the cellulose employed as initial material in the presence of large proportions of basic substances as sodium hydroxide, it is possible to obtain a rapid reaction on the water bath, the reaction temperature rising above 130°.

In an application filed in the United States March 14, 1913, which was divided, and Divisional Applications filed October 20, 1913<sup>1</sup>, L. Lilienfeld recapitulated the subject

1. U. S. P. 1217027, 1917; abst. C. A. 1917, **11**, 1545; J. S. C. I. 1917, **36**, 383. U. S. P. 1217028, 1917; abst. J. S. C. I. 1917, **36**, 383; Mon. Sci. 1918, **85**, 4. E. P. 6387, 1913; abst. C. A. 1914, **8**, 2947; J. S. C. I. 1914, **33**, 417; Kunst. 1914, **4**, 236, 256. F. P. 459972, 1913; abst. C. A. 1914, **8**, 3373; J. S. C. I. 1913, **32**, 1153; Chem. Ztg. 1913, **37**, 1293; Chem. Ztg. Rep. 1914, **38**, 394; Kunst. 1914, **4**, 75. Aust. P. 73001; abst. Kunst. 1917, **7**, 222. Aust. P. 62809, 1913; abst. Chem. Ztg. 1913, **37**, 1499. Hung. P. Appl. L-3294; abst. Chem. Ztg. 1913, **37**, 11. Ital. P. 173413, 183582.

matter of his former patents, and pointed out the use of the methyl-, ethyl- and propyl-celluloses for many technical applications, especially in the formation of plastics and artificial filaments, and the use of alkylcelluloses for plastic formation in conjunction with camphor, naphthalene, phenol phosphates, nitromethane, and similar plastic-inducing bodies for celluloids manufacture.

For artificial filament formation, the cellulose ethers are dissolvable in benzene, alcohol, alcohol-benzene, either alone or combined with nitrocellulose or cellulose acetate, and extruded through jets in the usual manner, the precipitating bath, of course, being selected as a non-solvent of the cellulose ether composition. For the preparation of lacquers, varnishes and paints, the cellulose ethers are dissolved, and oils, fats, waxes and other softening and plasticizing agents incorporated therewith. In the formation of films, it is recommended to dissolve the cellulose ether in an appropriate low boiling solvent combination, clarify by filtration, and then cast on a wheel or endless band in the usual way.

In 1920 Wedorf<sup>1</sup> prepared a resume of the Lilienfeld patents which had appeared up to that time, with brief references to the work of Denham and Woodhouse, and this was published in English by C. West<sup>2</sup>.

**First Disclosures of Dreyfus.** On November 18, 1912, the French Patent Office officially received and accepted a disclosure for the manufacture of cellulose ethers and products derived therefrom of Henry Dreyfus<sup>3</sup>, in which he points out that while it is comparatively simple to effect the etherification of hydroxyl groups, on the contrary it is

1. *Kunst.* 1920, **10**, 112-115; *Chem. Zentr.* 1920, IV, 753; *Chim. et Ind.* 1921, **5**, 332; *C. A.* 1920, **14**, 2551.

2. *Paper*, 1920, **26**, 15.

3. *F. P.* 462274, published Jan. 23, 1914; *abst. J. S. C. I.* 1914, **33**, 248; *C. A.* 1914, **8**, 3859; *Chem. Ztg. Rep.* 1914, **38**, 349; *Rev. Chim. Ind.* 1914, **25**, 81.

not so easy to etherify cellulose and its derivatives, on account of the fact that the known methods for etherifying hydroxyl groups as employing an alcohol in the presence of a condensing substance as sulfuric acid, potassium bisulfate or hydrochloric acid cannot be used successfully on account of the adverse action on the cellulose molecule.

Secondly, etherification in the presence of alkalis in solution is not very effective, for example in a dilute solution of soda a salt of cellulose is not formed, for in the presence of water the salt is decomposed into its components, so that the etherifying agent which does not act on the free soda is without effect on the cellulose.

If on the other hand, one employs an excess of soda in order to impell the formation of cellulose salts, there is required an enormous excess of etherifying agent, so that such processes are of no industrial value, and the decomposition of the salt takes place at the same time. In this invention, Dreyfus states that he has found that a perfect and simple method of producing the true ethers of cellulose as methyl or ethyl ethers results, if one effects the reaction by the aid of alkalis such as sodium or potassium, by employing for each molecule of cellulose, from two to four molecules of soda or potash diluted as by water or other solvent.

The dilution of the alkali should be such as to permit of complete impregnation of cellulose, and in afterwards drying to a definite alkali percentage, the alkali is found distributed uniformly throughout the cellulose mass. After impregnation, the excess water is removed as by vacuum evaporation, aided by heat if desired. This "salt of cellulose" in the anhydrous condition is unable to decompose on account of the absence of moisture, while the alkali remains in the hydroxyl groups. It therefore is impossible for etherification to take place other than by attacking the hydroxyl groups of the cellulose.

In employing methyl chloride or ethyl chloride as etherifying agent, the reaction takes place in a closed vessel without the addition of other solvents or diluents on account of the fact that the etherifying agent is added below its boiling point, the reagents being uniformly mixed during the course of the reaction. If a too elevated temperature be used, as above  $100^{\circ}$ , the cellulose itself will be partially decomposed in such a manner as to result in the formation of useless products. It is preferable to use a slight excess of alkali in order to prevent an acid reaction, which has an unfavorable effect on the cellulose.

If on the other hand, one employs methyl or ethyl sulfates which represent etherifying agents *par excellence*, the etherifying reaction may be carried out more smoothly and uniformly by the introduction of a diluent as benzene, ordinary or moderate temperatures only, being employed. At the close of the etherification process, the cellulose ether is separated in any known manner, the products obtained being distinguished by their solubility in organic solvents. By employing the appropriate solvents the course of the reaction may be so directed that the cellulose ether goes into solution during the etherification.

It has thus been found that in submitting the cellulose ethers to a further treatment, for example with dilute acids or their salts, one is able to successively modify the solubility of the cellulose ethers in different solvents, or by interrupting the reaction at various stages. The products thus obtained may be transformed by means of various solvents into celluloid, films, artificial silk, artificial horsehair or analogous products, and for the same uses as those now employed for cellulose acetate.

**Investigations of Denham and Woodhouse, 1913-1914.**  
In order to further test the correctness of the view that had been maintained, that the cellulose molecule is composed wholly of dextrose residues as seemed to have been

definitely established by R. Willstaetter and L. Zechmeister<sup>1</sup> on the action of concentrated hydrochloric acid as the hydrolytic agent for the conversion of cellulose to dextrose, and to confirm the results of H. Ost<sup>2</sup> on the high yields of the acetates of dextrose and cellulose obtained by the acetolytic method of degradation and which point to the same conclusion, W. Denham and H. Woodhouse attacked the problem from the viewpoint of a study of the etherification products of cellulose, especially those bodies resulting from methylation, and published their first memoir in the Journal of the London Chemical Society in September, 1913,<sup>3</sup> following this with a communication in the transactions of the same journal the year following<sup>4</sup>. This is the first comprehensive publication on etherified celluloses.

As the initial step, the authors tried various methods for the methylation of cellulose, and found that methylation may be effected simply by the action of methyl sulfate on the fibrous cellulose after it has been impregnated with a 15% solution of sodium hydroxide. Under the conditions adopted, the reaction appears to proceed in well defined stages, and, notwithstanding the use of NaOH in quantity somewhat greater than that represented by the ratio  $C_6H_{10}O_5:2NaOH$ , and of excess of methyl sulfate over that required for the alkali, the composition of the cellulose ether formed is that of a substance of the empirical formula  $C_{12}H_{19}O_9.OMe$ . If the etherification with NaOH and methyl

1. Ber. 1913, **46**, 2401; abst. J. S. C. I. 1913, **32**, 822; C. A. 1913, **7**, 3412; J. C. S. 1913, **104**, i, 955; J. Soc. Dyers. Col. 1913, **29**, 326; Bull. Soc. Chim. 1913, **14**, 1354; Chem. Zentr. 1913, **84**, II, 1209.

2. Ann. 1913, **398**, 313; abst. J. S. C. I. 1913, **32**, 784; Kunst. 1913, **3**, 352; C. A. 1913, **7**, 3836; J. C. S. 1913, **104**, i, 446, 833, 1148; Chem. Zentr. 1913, **84**, II, 2035; Ber. 1913, **46**, 2995.

3. J. C. S. 1913, **103**, 1735; abst. C. A. 1914, **8**, 243; J. S. C. I. 1913, **32**, 974; Ann. Rep. Soc. Chem. Ind. 1913, **10**, 88; Bull. Soc. Chim. 1913, **14**, 1495; Chem. Zentr. 1913, **84**, II, 1857; Chem. Ztg. Rep. 1914, **38**, 241; Meyer Jahr. Chem. 1913, **23**, 536. Cellulose Chem. 1920, **1**, No. 2, 14; No. 3, 22; Paper 1920, **27**, No. 11, 19.

4. J. C. S. 1914, **105**, 2357; abst. C. A. 1915, **9**, 203; J. S. C. I. 1914, **33**, 1084; Ann. Rep. Soc. Chem. Ind. 1914, **11**, 93; Bull. Soc. Chim. 1915, **18**, 199; Chem. Zentr. 1915, **86**, I, 81; Cellulose Chem. 1920, No. 2; Paper 1920, **27**, No. 11, 19.

sulfate is repeated, the new compound has the composition represented by the formula  $C_6H_9O_4.OMe$ , while the substance produced on a third treatment is more nearly represented by the less simple formula  $C_{24}H_{35}O_{15}(OMe)_5$ . Corroborative results were obtained in several series of experiments, the ether having not been subjected to a fourth methylation.

Although the products obtained at the different stages may be adequately represented by the comparatively simple empirical formulae above given, there is basis for speculation respecting the relative activity of the different hydrogen atoms in the cellulose molecule afforded by the degradation incident to the methylation treatment.

The methylated celluloses retain the fibrous structure of the original material (i.e., the methylated celluloses produced are not soluble in the etherifying medium in contradistinction to the cellulose esters, the acetates of which dissolve in the acetylating bath unless a non-solvent is purposely introduced), but with increasing increment of methyl radicals, the dried substance becomes more and more horny in appearance. The first product is readily soluble in cuprammonium solutions, the others less readily. Apparently only the first product dissolves in zinc chloride solution, but all of the methylated celluloses may be acetylated. That the methoxyl group exists in a state of combination is shown by the high temperature ( $120-130^\circ$ ) to which they must be heated with hydriodic acid during the methoxyl determination by Zeisel's method before a precipitate forms in the silver nitrate solution, and this fact is further established by the persistence of the methoxyl group during subsequent reactions.

The product,  $C_{12}H_{19}.OMe$ , undergoes a slight change in composition when treated with 15% NaOH solution, the recovered substance showing a diminished percentage of carbon, hydrogen, and, possibly of methoxyl. The product from the methylation,  $C_6H_9O_4.OMe$ , may be converted into



a xanthate by treatment with sodium hydroxide solution and carbon bisulfide in a manner similar to the usual production of viscose from ordinary cellulose. The methylated cellulose regenerated from the filtered solution by warming on the water bath has a slightly less methoxyl content than the original substance. The formation of methylated viscose has a direct bearing on the question of the relative reactivity of the hydrogen atoms of cellulose, for, if the most reactive hydrogen atom of the unit  $C_6H_{10}O_5$ , is replaced in ordinary viscose from cellulose by the  $CS.Na$  group, and in the methylated cellulose by the methyl group, it is obvious (if the compositions of the xanthates are similar), that xanthate from ordinary cellulose must involve in its formation a different hydrogen atom or atoms from that which is concerned in the formation of the xanthate from methylated cellulose.

The methylated celluloses, when acted upon by a mixture of acetic acid and anhydride which contains a trace of sulfuric acid, give acetyl derivatives, readily soluble in chloroform, and show some resemblance to acetylcellulose. Analyses of the products, however, show that they contain less carbon, hydrogen and methoxyl than would normally be present in completely acetylated derivatives of the methylated celluloses, but the analytical figures do not indicate that acetylation is incomplete, but do indicate that partial elimination of methoxyl has occurred, perhaps accompanied with degradation of the cellulose molecule with consequent degree of acetylation than if no such change had taken place. Two of the analyzed samples indicated partial decomposition.

The cellulose used was (1) calico—a sample of madder bleached calico, as a typical “normal” cellulose, and (2) ordinary cotton wool. The calico was beaten under water to thoroughly disintegrate the fiber.

In general, the cellulose was subjected to the following treatment: The preparation of alkali-cellulose was carried

out by soaking cotton for several days in three to four times its weight of 15%-17% NaOH solution, the proportions of cellulose to sodium hydroxide being approximately  $C_6H_{10}O_5 \cdot 2NaOH$ , but a slightly larger amount of sodium hydroxide was usually present. On addition of the amount of methyl sulfate required to react with the NaOH, reaction takes place with evolution of heat, but the cooled mixture is still alkaline, and remains so even upon gentle warming unless a considerable excess of methyl sulfate has been added. The product was successively washed several times with water, then with dilute alkali and with acid and finally with water, and the water removed by vacuum drying at  $120^\circ$  until constant in weight. Subsequent treatments with NaOH and methyl sulfate were similarly carried out.

In the first treatment of the cellulose, 50 gms of the disintegrated material previously dried at  $100^\circ$ , were soaked in 200 cc. NaOH 15%, allowed to remain 3 days with frequent stirring, then 52 gms methyl sulfate added. After subsidence of the heat of reaction, an additional 10 gms methyl sulfate was added to the alkaline mixture, and the mixture shaken with 500 cc. benzene, the alkaline reaction still persisting. It is inadvisable to use benzene as a solvent for methyl sulfate on account of the formation of a persistent emulsion, and in subsequent experiments this difficulty was overcome by using a large excess of methyl sulfate. The cotton fabric gave 4.63% methoxyl, and the fibers, 9.29% and 10.14% respectively. The cotton wool similarly treated, showed 8.5% and 9.29% methoxyl.

In the second treatment 43 gms crude product from the first treatment were allowed to stand  $1\frac{1}{2}$  days with 170 cc. NaOH 15%, and a quantity of methyl sulfate calculated on the NaOH added. After 3 weeks standing the alkaline mixture was neutralized with HCl, washed and dried. The fabric gave 7.08% methoxyl, the fibers 16.77% and 17.62% respectively. Cotton gave 17.62% and 19.72% methoxyl.

In the third treatment the loose calico fibers only were treated, these when dry form a horny mass, penetrable by NaOH solution only with difficulty. Two distinct preparations were carried out, the quantities used being (1) 12 gms of the twice methylated product, 33 cc. NaOH 17%, and 30 gms methyl sulfate. In (2) there was used 2 gms of the twice methylated cellulose, 8 cc. NaOH 15% solution and 12 gms methyl sulfate. The results for (1) are 21.53% methoxyl, and (2) 22.11%. In the use of cotton wool, 20 gms of the twice methylated ether, after remaining 2 days in contact with 54 cc. NaOH 17%, were treated with 11 gms methyl sulfate, the yield being 73% of the calculated amount. Methoxyl, 21.59% and 23.3% respectively.

In studying the action of NaOH on the product from the first methylation of cotton wool, 2 gms of the dried product were soaked for 4 days with 8 cc. NaOH 15%. After washing and drying the substance weighed 1.68 gms and contained 7.8% methoxyl, the methoxyl content being 8.5% before treatment.

In conversion of the twice methylated product from cotton wool into xanthate, and regeneration of methyl cellulose therefrom, 8 gms carbon bisulfide were added to a mixture of 10 gms methylated cellulose, and 30 gms NaOH 18%, which had been in contact with each other for 24 hours, the whole being allowed to stand together for 6 hours with frequent stirring. After exposure to the air for a few minutes to allow free  $\text{CS}_2$  to dissipate, the mass was brought into solution by prolonged stirring with 30 cc. NaOH 18%. After filtration, the methylcellulose was regenerated by heating the solution on the water bath, and washed. Methoxyl, 14.08% and 15.64%. The methylated cellulose used contained 19.72% methoxyl.

In the acetylation of methylcelluloses derived from cotton wool after the first, second and third methylations in each instance 2 gms of methylated cellulose were treated with a mixture of 8 gms acetic anhydride, 8 gms acetic acid

and a trace of sulfuric acid, the temperature being kept below 30°. After the mixture had remained about 12 hours at ordinary temperature, it was warmed to 35° for a few minutes, diluted with acetic acid, filtered and precipitated in a large bulk of water<sup>1</sup>. The acetyl content from the first two methylations was found to be 54.74%, 46.15%, and the methoxyl content from the three methylations, 5.66%, 11.29% and 15.32% respectively<sup>2</sup>.

In the second communication published in 1914, in which a repetition of the work previously described was undertaken with a larger quantity of material, the well-marked stages observed in the first and second methylation treatments were less apparent. In the following table is a comparison of the amounts of methoxyl group (methoxyl) in the products from each successive treatment in one of the series of experiments previously detailed (1), with those in the products at the corresponding stages in a newer series (2):

	Concentration of NaOH	Percentage methoxyl after				
		1st	2nd	3rd	4th	5th treatments
(1)	15-18 gms per 100 cc.	8.5	19.7	23.3	25.5	24.6
(2)	17 gms per 100 cc.	5.3	11.5	14.0	18.7	20.7

1. W. Schleimann, Ann. 1911, **378**, 366; abst. Zts. ang. Chem. 1912, **25**, 771; Bull. Soc. Chim. 1911, (4), **10**, 1346; C. A. 1911, **5**, 1276; Chem. Zentr. 1911, **82**, I, 807; J. S. C. I. 1911, **30**, 126.

2. In a note attached to their original article, the authors state: "During the progress of this work, and after most of the results just recapitulated had been reported to the Carnegie Trust, an abstract of a patent dealing with similar problem was published (J. S. C. I. 1913, **32**, 420). In the full specification (F. P. 447, 974, published Jan. 20, 1913), Lillienfeld describes the preparation of cellulose ethers (ethyl-celluloses) by the action of ethyl sulfate on solutions of regenerated cellulose in concentrated sodium hydroxide solution. It is stated that substances of various degrees of ethylation can be prepared, and that the products are soluble in organic solvents or in some cases, even in water; analytical figures (for carbon and hydrogen) are given for a substance of the composition,  $C_{12}H_{12}O_6(OEt)_x$ . The manner of preparation of these substances and their range of solubility suggest that the cellulose molecule has undergone considerable degradation. The authors, on the other hand, have endeavored to carry out the methylation with as little degradation as possible of the cellulose complex, ..." Experiments conducted on lines similar to those described above have also been carried out by the authors on starch, the results showing that the starch molecule similarly undergoes normal methylation.

The divergences between the methoxyl contents at corresponding stages in the two series, due perhaps to a variation in concentration of alkali and to differences in quantities of material operated upon, clearly indicate that the agreement previously observed between simple formulae and composition of the methylated cellulose is fortuitous; a study of the products of the hydrolytic decomposition of methylated cellulose pointing to the same conclusion.

The yields at each stage of Series 2 in the foregoing table indicate that but little of the methylated cellulose had dissolved in the wash water, but, on repeating the process for a sixth time, a considerable quantity of material was found to have passed into solution. This may be accountable on the grounds that a much more concentrated sodium hydroxide solution was employed.

Hydrolysis of the methylated cellulose was carried out on the undissolved portion from the final treatment, which contained about 25% methoxyl, and was brought about by the use of concentrated hydrochloric acid according to the method of R. Willstaetter and L. Zechmeister<sup>1</sup> for the hydrolysis of cellulose. The process yielded a mixture of methylated hexoses, a trimethyl hexose being obtained in the crystalline state, and appears to be a true methylated glucose, since it displays practically identical rotation in all solvents, and this property, as pointed out by J. Irvine and T. Hogg<sup>2</sup> is characteristic of the glucose configuration. The various hydrolytic products isolated are classified as:

- (1) Amorphous monomethyl glucose or mixture of monomethyl glucoses.
- (2) Amorphous dimethyl glucose, or mixture of dimethyl glucoses.
- (3) Crystalline trimethyl glucose.
- (4) Trace of crystalline matter resembling tetramethyl glucose.

1. Ber. 1913, **46**, 2401.

2. J. C. S. 1914, **105**, 1386; Proc. Chem. Soc. 1914, **30**, 145; abst. C. A. 1914, **8**, 2682; J. S. C. I. 1914, **33**, 657; Bull. Soc. Chim. 1914 (4), **10**, 899; Meyer Jahr. Chem. 1914, **24**, 204.

The products of hydrolysis were resolved by a complex series of fractionations with solvents (ether and acetone) and by distillation. Substantially, the highest product of the methylation of cellulose is represented by trimethyl glucose after hydrolysis, which confirms the existence of three free OH groups in the  $C_6$  unit. As the trimethyl glucose readily crystallized and was apparently a homogeneous substance occurring in the  $\alpha$ -form, there is presumption in favor of the symmetrical linkage of the dextrose residues in the cellulose molecule. The trimethyl-glucose isolated, in the crystalline form amounted to 10% of the crude product, and a further quantity remained in the mother liquors. It did not yield an osazone.

The methylated cellulose subjected to hydrolysis was prepared by impregnating cotton wool (1 equivalent of  $C_6H_{10}O_5$ ) with 2 mols. NaOH in solution, and adding methyl sulfate in portions to the mixture until the alkaline reaction disappeared, this requiring about  $1\frac{1}{2}$  times the quantity of methyl sulfate calculated to react with the NaOH present. The mixture became warm during the reaction. The product from five consecutive similar treatments in which the NaOH solution contained 17 gms per 100 cc. was finally (6th treatment) soaked for a week under diminished pressure in NaOH solution 38.3 gms in 100 cc. and then treated with sufficient methyl sulfate to neutralize the alkaline reaction, this requiring four times the calculated quantity of methyl sulfate.

The results obtained are reproduced in the following table:

1st treatment.	103 gms cotton	gave	101 gms OMe,	5.28%
2nd treatment.	99.5 "	"	95 "	11.48%
3rd treatment.	92 "	"	86 "	13.98%
4th treatment.	83 "	"	79 "	18.74%
5th treatment.	74 "	"	68 "	20.69%
6th treatment.	65 "	"	45.6 "	23.89%
				25.97%

The methylated cellulose hydrolyzed was the final product from the above etherifications, and contained 23.89%-25.97% methoxyl. It gelatinized when added at 0° to an aqueous solution of HCl which had been saturated at that temperature, and dissolved in a few hours to a nearly colorless solution.

In 1917 these investigators<sup>1</sup> published the culmination of their work on trimethylglucose, in comparison with the work of J. Irvine, A. Fyfe and T. Hogg<sup>2</sup>, but of minor interest in this connection.

In 1921 appeared Part III of this work<sup>3</sup> on the methylation of cellulose, in which etherifications has yielded 44.6% methoxyl, approaching closely to the 45.6% of methoxyl required by theory for trimethylcellulose. The slow rate of increase in the methoxyl content in the final stages of methylation is indicative that the limit has been closely approached. That these ethers retain a high degree of complexity is apparent by the almost complete absence of copper-reducing property in a product containing about 40% methoxyl, in which, as in more highly methylated preparations, the fibrous structure of cellulose persists. Further, the displacement of hydrogen by methyl groups does not confer solubility in such solvents as alcohol, acetone or chloroform.

The solubility of methylated cellulose in Schweitzer's reagent appears to decrease with increasing methoxyl content, and products containing about 40% methoxyl are insoluble. The question of the homogeneity of methylated cellulose is of prime importance in relation to deducing the

1. J. C. S. 1917, **111**, 244; abst. C. A. 1917, **11**, 1953; J. S. C. I. 1917, **36**, 607; Chem. Zentr. 1918, **89**, I, 80.

2. J. C. S. 1915, **107**, 524; abst. C. A. 1915, **9**, 1907; J. S. C. I. 1915, **34**, 627; Chem. Zentr. 1915, **86**, II, 267; Meyer Jahr. Chem. 1915, **25**, 108.

3. W. Denham, J. C. S. 1921, **119**, 77; abst. C. A. 1921, **15**, 1698; J. S. C. I. 1921, **40**, 211A; Ann. Rep. Soc. Chem. Ind. 1921, **6**, 133; Bull. Soc. Chim. 1921, (4), **30**, 425; Chem. Zentr. 1921, **92**, I, 892; Cellulose Chem. 1921, **2**, No. 6, 74; Caout. et Gutta. 1922, **19**, 11379.

constitution of cellulose from the nature of the hydrolytic products. It was found that several preparations of methylcellulose when treated with Schweitzer's reagent so that only a portion was dissolved, yielded a residue with a methoxyl content greater than that of the untreated substance. The degree of homogeneity is ascribed to the manner of preparation of the methylcellulose; for material of low average methoxyl content it was greatest where concentrated alkali had been employed, possibly owing to an unequal penetration of the cotton by the alkali. This emphasizes the necessity, in commercial production of cellulose ethers, of care in the formation of the intermediate step of alkali-cellulose formation, a fact keenly appreciated in the viscose rayon industry.

The most homogeneous methylcellulose was one in which an ethereal solution of methyl sulfate was employed, and the best yields,—apparent in an increased weight of cellulose ether after methylation—when ether was present. A preparation containing about 40% of methoxyl gave indications of lack of uniformity explicable from its history; one containing 42% methoxyl was insoluble in Schweitzer's reagent, alcohol, acetone and chloroform.

As the limit of etherification is approached, irregularities in methylation become less apparent. In one series, 100 gm. cotton gave 104 gms. methylcellulose containing 31.3% methoxyl corresponding to a 91% yield on the theoretical. This product had undergone four separate methylations. The conclusion seems to be justified from the experimental data that the limit of methylation of cellulose lies in the neighborhood of that required for trimethylcellulose, and that a methylcellulose of this limiting methoxyl content can be prepared which is representative of the whole of the original cellulose.

The pertinent (in this respect) experimental data is as follows:



I. *Methylcellulose of 20.4% methoxyl.* 20 gms. solid NaOH in 100 cc. solution. No solvent was employed for the methyl sulfate, slightly more of which was used than is represented by the ratio  $\text{Me}_2\text{SO}_4.\text{NaOH}$ . In each stage the temperature rose to  $70^\circ$  during the reaction, and the mixture was afterwards gently warmed until acid throughout.

*First Stage.* 105 gms. cotton, 500 cc. NaOH solution, 390 gms. methyl sulfate. Yield, 135 gms.

*Second Stage.* 135 gms. of product from the first stage, 400 cc. NaOH solution, 236 gms. methyl sulfate. Yield, 98 gms. Methoxyl 20.4%.

*Action of Schweitzer's Reagent.* The product from the second stage, after remaining for several days with 4 liters Schweitzer's reagent, left 42 gms. undissolved residue containing 22.7% methoxyl. Three quantities of 3 gms. each, containing 22.7% methoxyl were again treated with 170 gms. Schweitzer's reagent. Residue after 2 days, 1.5 gms., methoxyl, 23.1%. After 5 days, 1.3 gms., methoxyl, 24.3%. After 7 days, 1.3 gms., methoxyl, 24.7%. The mixed residues were entirely soluble in Schweitzer's reagent.

By the action of Schweitzer's reagent on 28 gms. of the substance containing 22.7% methoxyl, 4.4 gms. undissolved residue were obtained which contained 23.4% methoxyl. This 4.4 gms. were again treated with Schweitzer's reagent so as to leave a small residue, which residue contained 28% OMe.

II. *Methylcellulose of 39.5 methoxyl.* This substance was prepared in nine stages. After three stages, in each of which the material was impregnated with half its weight of NaOH added as a solution containing 21.4 gms. solid in 100 cc., the OMe content was 24.8%. In all the stages, somewhat less methyl sulfate was employed than is represented by the ratio  $\text{Me}_2\text{SO}_4.\text{NaOH}$ , and the product was alkaline at the close of the reaction. From 160 gms. cotton were obtained 135 gms., yield 79% of that obtainable of a product having OMe, 24.8%. The percentage of methoxyl

remained stationary from the eighth to the ninth stage (OMe, 39.7%-39.5%).

*Action of Schweitzer's Reagent.* 2.8 gms. of methylcellulose containing 39.5% OMe, after treatment for 4 days with 50 cc. Schweitzer's reagent, gave 2.6 gms. undissolved residue of 40% OMe. 2.4 gms. of this residue on further treatment with Schweitzer's reagent, were reduced to 2.2 gms., with 40.4% OMe.

*Copper Reduction.* 0.978 gms. of substance (OMe, 39.5%) was treated with Fehling's solution. Cuprous oxide, 0.11%.

III. *Preparation of Methylcellulose using Ether.* 100 gms. cotton was soaked 1 day in 1000 cc. NaOH 20%, so that 350 gms. of the solution (containing 70 gms. NaOH) were left. 100 cc. methyl sulfate and 700 cc. ether was heated under reflux for several hours, and the ether removed by distillation. The weight of the washed and dried product was 105 gms.

*Action of Schweitzer's Reagent.* From 2.88 gms. of this substance (OMe, 31.3%) after immersion in 100 cc. Schweitzer's reagent for 3 hours, gave 1.93 gms. undissolved of 32.4% OMe. 88 gms. methylcellulose (OMe, 15.6%) which had been made in one stage, using ether, were immersed in 600 cc. Schweitzer's reagent 3 days, when 8.4 gms. undissolved material were recovered of 15.2% OMe.

IV. *Methylcellulose containing over 40% Methoxyl.* Highly methylated products were prepared by variants of the methods above described. For one of these, the following analytical figures were obtained: C, 52.19; H, 7.63; OMe, 44.6. Trimethylcellulose,  $C_9H_{16}O_5$ , requires C, 52.9, H, 7.84, OMe, 45.6.

*Action of Solvents.* The behavior of a methylcellulose containing OMe 42% was examined towards alcohol, acetone and Schweitzer's reagent. 1.8802 gms. after being

extracted with alcohol for 3 hours, afterwards weighed 1.879 gms. The same sample was then extracted in the same manner with acetone for 3 hours, and weighed 1.879 gms. 0.408 gms. of this, immersed in Schweitzer's reagent for 24 hours gave 0.407 gms. undissolved.

A repetition of a portion of the above work was carried out in 1922 by J. Irvine, W. Denham and E. Hirst<sup>1</sup>, in which the methylation was repeated 20 times, giving a cellulose containing 43% methoxyl, as compared with a theoretical value of 45.6% for a trimethylcellulose. The methoxyl value previously obtained (25%) is less than that required for a dimethylcellulose (32.6%), and on hydrolyzing the product a mixture of methylated glucoses resulted, 2.3.6—trimethylglucose being isolated. In repeating the work, the carbon and hydrogen values found agree with the formula  $(C_6H_7O_3 [OMe]_3)_x$ , and as the material preserved a fibrous structure, it was assumed that profound molecular alteration had not taken place.

The trimethylcellulose was heated with a large excess of methyl alcohol containing 1% hydrochloric acid for 50 hours at 125-130°, the treatment effecting depolymerization, hydrolysis, and conversion of the scission products into the corresponding methylglucosides. The various fractions when collected, contained trimethyl-methylglucoside with a small proportion of dimethyl-methylglucoside, the small quantity of the latter agreeing exactly with the deficiency of 2.6% in the methoxyl content of the trimethylcellulose used. No trace of tetramethyl-methylglucoside was found, and the conclusion was reached that trimethylcellulose gives 2.3.6-trimethylglucose as the only product. The authors conclude that this affords a proof that all the glucose residues in  $\alpha$ -cellulose are identical in structure, and the simplest possible formula that will satisfy this condition is that of a 1.4-anhydroglucose.

1. Chem. Trade J., 1922, **71**, 291; abst. C. A., 1923, **17**, 1713.

**Advancement in the Cellulose Ether Art, 1915-1920.**

The previous investigations of Denham and co-workers, and the patent applications of Leuchs, Lilienfeld and Dreyfus had shown that the cellulose ethers may be formed by the substitution of an alkyl or aryl radical in place of a hydroxyl hydrogen atom in cellulose, and that methylcelluloses and ethylcelluloses are bodies, in general, of high stability, difficult of saponification, and with a wide range of solubility, dissolving, as they do, in the same classes of solvents as the nitrocelluloses and cellulose acetates, yet interest was not keen and progress seemed slow. Notwithstanding that many industrial possibilities were indicated from the patent descriptions, the great drawback at this time to their entering the field as direct competitors of the acetated celluloses was the high manufacturing cost due to the enormous amount of the relatively expensive methyl sulfate and ethyl sulfate required for their etherification to the point of solubility in the usual range of cheap commercial solvents, it having been found that the etherification process must be carried to the maximum point of introduction of alkyl or aryl groups into the cellulose aggregate, in order to obtain satisfactory solubility, tensile strength and stability.

It has been established that the typical etherification reaction, such as involved in the formation of pentaethylcellulose may be expressed as follows: 2 molecules regenerated cellulose,  $C_6H_{10}O_5$ , plus 5 molecules sodium hydroxide,  $NaOH$ , give 1 molecule soda cellulose (alkalicellulose),  $C_{12}H_{15}O_{10}Na_5$  and 5 molecules of water. One molecule of soda cellulose then reacts with 5 molecules ethyl sulfate,  $(C_2H_5)_2SO_4$ , to form pentaethylcellulose,  $C_{12}H_{15}O_{10}(C_2H_5)_5$  and 5 molecules sodium ethyl sulfate,  $Na(C_2H_5)SO_4$ , there being a secondary reaction whereby 3 molecules ethyl sulfate and 3 molecules sodium hydroxide gives rise to 1 molecule diethyl ether,  $(C_2H_5)_2O$ , 1 molecule ethyl alcohol,  $C_2H_5OH$ , 3 molecules of sodium ethyl sulfate and 1 molecule of water. Or, combining the reactions, we have 2

molecules cellulose, 8 molecules sodium hydroxide and 8 molecules ethyl sulfate, give 1 molecule pentaethylcellulose, 8 molecules sodium ethyl sulfate, 1 molecule each diethyl ether and ethyl alcohol and 6 molecules water.

In practically carrying out the above reaction, the ethylcellulose is precipitated by the addition of a non-solvent thereof and recovered by filtration, the sodium ethyl sulfate by drying down the first portion of the filtrate, and the ether and alcohol as distillate from the reaction.

H. Clarke<sup>1</sup> received patent protection for a combination of ethylcellulose with the sulfones as a plastic composition especially useful for film manufacture and varnish production, as the solutions are transparent, and when evaporated to dryness give strong and flexible sheets. *n*-Dibutyl-, diisobutyl-, diethyl-, dimethyl-, *n*-dipropyl-, diisopropyl-, diisoamyl-, methylethyl-, diheptyl-, ethylisoamyl-, and diphenyl-sulfone are specified, used either singly or in conjunction.

The Deutsche Celluloid Fabrik<sup>2</sup> interact cellulose or alkalicellulose with the copper, aluminum or lead salts of cellulose acetic acid or cellulose propionic acid to form products as substitutes for gelatin. H. Dreyfus<sup>3</sup> prepares benzylcellulose, ethylbenzylcellulose and methylbenzylcellulose by the action of benzyl chloride alone or in conjunction with methyl sulfate or ethyl sulfate, or alternately with them upon modified cellulose. He first called attention to the

1. U. S. P. 1357614; abst. C. A. 1921, **15**, 436; J. S. C. I. 1921, **30**, 7A; Rev. Prod. Chim. 1922, **25**, 277; Chem. Tech. Uebers. 1921, **45**, 99; Paper, 1921, **27**, No. 20, 26; No. 21, 27; Caout. et Gutta. 1921, **18**, 11074.

2. D. R. P. 332203; abst. C. A. 1921, **15**, 2184; J. S. C. I. 1921, **40**, 344-A; Ann. Rep. Soc. Chem. Ind. 1921, **6**, 188; Kunst. 1921, **11**, 94; Chim. et Ind. 1922, **8**, 426; Chem. Tech. Uebers. 1921, **45**, 59; Chem. Zentr. 1921, **92**, II. 672.

3. U. S. P. 1451331; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1927, **46**, 447-A; E. P. 164377; abst. C. A. 1922, **16**, 493, 494; Chem. Met. Eng. 1921, **25**, 714; J. S. C. I. 1921, **40**, 540-A; Chem. Tech. Uebers. 1921, **45**, 327. Belg. P. 290448. E. P. 164375; abst. J. S. C. I. 1921, **40**, 540-A.

observation<sup>1</sup> that the cellulose ethers, especially the methyl and ethyl derivatives, are analogous to cellulose acetates in the sense that the percentage alkyl content is no criterion of their physical properties, especially solubility ratios. He prepares the methyl and ethyl ethers with cellulose conversion products in the presence of alkali and suitable alkylating agent under such conditions that the quantity of water present or added (disregarding the water formed during the process), is at no stage of etherification greater than about four times the weight of cellulose, and preferably is not greater in amount than 0.5-1.5 times this weight. And also, that the total quantity of alkali is at least equal to, and preferably exceeds, 3-19 times the weight of water present or added. The ethers obtained are characterized by their insolubility in hot or cold water, and are not precipitated from alcoholic solution by alcoholic solutions of alkali.

As a serviceable agglutinant for the cellulose ethers which are powerful solvents, insoluble in water, non-volatile and which produce more or less solid solutions, the Farbenfabriken vorm. F. Bayer & Co.<sup>2</sup>, recommend the use of

1. E. P. 164374; abst. C. A. 1922, **16**, 493; J. S. C. I. 1921, **40**, 540-A; Ann. Rep. Soc. Chem. Ind. 1921, **6**, 138; Chem. Tech. Uebers. 1921, **45**, 327; Chim. et Ind. 1922, **8**, 654. F. P. 522613. Belg. P. 290449.

2. E. P. 115855; abst. Chim. et Ind. 1919, **2**, 93. D. R. P. 307125; abst. J. S. C. I. 1920, **39**, 400-A; Chem. Zentr. 1920, **91**, II, 505; Wag. Jahr. 1919, **65**, II, 354; Ann. Rep. S. C. I. 1920, **5**, 160; Chem. Ztg. Rep. 1920, **44**, 216. (Patent cites H. Dreyfus, E. P. 20975, 1911; abst. C. A. 1913, **7**, 890; J. S. C. I. 1913, **32**, 19; Kunst. 1913, **3**, 215.) D. R. P. 322619; abst. C. A. 1921, **15**, 2185; J. S. C. I. 1920, **39**, 719-A; Kunst. 1920, **10**, 182, 222; Chim. et Ind. 1923, **9**, 770; Chem. Tech. Uebers. 1921, **45**, 59; Chem. Zentr. 1920, **91**, IV, 417. D. R. P. 322648; abst. J. S. C. I. 1920, **39**, 719-A; Chem. Ztg. 1920, **44**, 342; Kunst. 1920, **10**, 220; Chim. et Ind. 1923, **9**, 770; Chem. Tech. Uebers. 1921, **45**, 104. (Same as Aust. P. Appl. A-2356, 1918; abst. Kunst. 1921, **11**, 184; Chem. Zentr. 1920, **91**, IV, 410.) F. P. 516900; abst. Rev. Prod. Chim. 1921, **4**, 713. A resorcinol acetate condensate with formaldehyde (D. R. P. 305516) has been advocated for artificial leather manufacture; resorcinol butylmethyl ketone (F. P. 468879) with formaldehyde as a celluloid substitute; resorcinoldiethyl ether (D. R. P. 358399) with formaldehyde condensate as a lacquer; resorcinol hexamethylenetetramine condensate combined with cellulose formate (D. R. P. 318509); resorcinol ketones (U. S. P. 1037158; E. P.

esters and ethers of phenols and naphthols, as *b*-naphthol-amyl ether, diethylresorcinol dicarboxylate (resorcine dicarboxylic acid diethyl ester), and especially resorcinol diacetate or *b*-naphtholamyl ether for ethyl-, propyl-, and benzyl-cellulose<sup>1</sup>. B. Gaisenband and C. Piestrak<sup>2</sup> have described and illustrated an apparatus said to be especially applicable for dissolving and filtering cellulose ether solutions. They<sup>3</sup> prepare cellulose ether compositions by adding a resin oil to the ether in the dissolved condition, in such proportions as required to give the desired transparency and flowable qualities. It is suggested that the resin oil be treated with alkali to remove the acid products and sodium acid sulfite to remove aldehydes, before adding to the cellulose ether solution. P. Goissedet<sup>4</sup> prepares new cellulose derivatives by acting upon cellulose with phenyl isocyanate in the presence of tertiary bases, cellulose phenylcarbamate being produced.

186107) as lacquer component; molded articles made with resorcinol (U. S. P. 922692, 924057, 965137, 925328, 1027121, 1114981; E. P. 208193); and resorcinol containing rubber substitute (U. S. P. 922692, 924057, 932318, 965137, 925328, 1027121, 1027122, 1037158, 1076417, 1245979; F. P. 486195; Can. P. 191262, 191263, 191427, 191428, 191562; Jap. P. 28327, 29247, 37857; Norw. P. 23365).

1. E. Zuehl, E. P. 17948, 1900; abst. J. S. C. I. 1900, **19**, 954; 1901, **20**, 926. U. S. P. 700884, 1902; abst. J. A. C. S. 1902, **24**, 520; Mon. Sci. 1903, **59**, 6. E. P. 8945, 1909; abst. J. S. C. I. 1909, **28**, 1271. F. P. 402038, 1909; abst. J. S. C. I. 1909, **28**, 1270; Mon. Sci. 1910, (4), **73**, 168. Knoll & Co. (D. R. P. 298806; abst. J. S. C. I. 1920, **39**, 483-A) combine resorcinol monoacetate with cellulose acetate. The Internationale Celluloseester Gesellschaft, D. R. P. 241963, 1908; abst. C. A. 1912, **6**, 2315; Chem. Tech. Rep. 1912, **36**, 110, have also patented the use of cellulose acetate as a filling or covering material in the construction of air craft. See this firm's D. R. P. 277529, 1909; abst. Kunst. 1914, **4**, 335, for use of resorcinol diacetate with acetated cellulose. Compare also Furst Guido Donnersmarck'sche Kunstseiden und Acetatwerke, Aust. P. 8165, 1902; Aust. Appl. 1905, 1909; Swiss P. 46329, 1909. For a description of the H. Dittmar process see D. R. P. 266384, 1911; abst. C. A. 1914, **8**, 2041.

2. F. P. 485068; abst. C. A. 1919, **13**, 1927; Rev. de Chim. Ind. 1917, **28**, 87.

3. F. P. 483316; abst. C. A. 1918, **12**, 995; 1922, **16**, 4063; Mon. Sci. 1918, **85**, 53; Rev. de Chim. Ind. 1916, **27**, 65.

4. U. S. P. 1357450; abst. C. A. 1920, **15**, 436; J. S. C. I. 1919, **38**, 714-A. E. P. 130277; abst. C. A. 1919, **14**, 122; J. S. C. I. 1920, **39**, 817-A. F. P. 496526; abst. Paper, 1921, **28**, 38.

W. Haworth<sup>1</sup> has disclosed a new method of preparing alkylated sugars, and has given physical constants for heptamethylsucrose, octomethylsucrose, tetramethyl- $\alpha$ -methylglucoside,  $\alpha$ -methylmannoside and its tri-, and tetra-derivatives, methylgalactoside, dimethylsalicin, and hydroxy- $\beta$ -methoxysuccinic acid<sup>2</sup>. W. Haworth and J. Law<sup>3</sup> hydrolyzed octomethylsucrose, tetramethylglucose and tetramethylfructose to alkylated derivatives. W. Haworth and G. Leitch<sup>4</sup> methylated maltose and maltoside, eight methoxyl groups being inserted in the maltose residue. The specific rotation of heptamethyl methylmaltoside was determined in methyl and ethyl alcohol, acetone and water.

K. Hess and W. Wittelsbach<sup>5</sup> in an exhaustive investigation upon the acetolysis of ethylcellulose under mild conditions, uniformly confirmed the deduction that when degradation has proceeded sufficiently far, the ethoxyl num-

1. Proc. Chem. Soc. 1914, **30**, 293; J. C. S. 1915, **107**, 8; abst. C. A. 1915, **9**, 1034; J. S. C. I. 1915, **34**, 241; Bull. Soc. Chim. 1915, (4), **18**, 300; Chem. Zentr. 1915, **86**, I, 881; Meyer Jahr. Chem. 1915, **15**, 109.

2. In this connection see T. Purdie and J. Irvine, J. C. S. 1903, **83**, 1021; 1905, **87**, 1028. J. Nef, Ann. 1914, **403**, 204. T. Purdie and R. Bridgett, J. C. S. 1903, **83**, 1037. J. Irvine and A. Moodie, J. C. S. 1905, **87**, 1465. J. Irvine and A. Cameron, J. C. S. 1904, **85**, 1071. J. Irvine and R. Rose, J. C. S. 1906, **89**, 814. L. Maquenne, Bull. Soc. Chim. 1905, (3), **33**, 469.

3. J. C. S. 1916, **109**, 1314; abst. C. A. 1917, **11**, 576; Bull. Soc. Chim. 1917, (4), **22**, 438; Chem. Zentr. 1917, **88**, I, 1076. Compare also W. Haworth, J. C. S. 1915, **107**, 8. T. Purdie and J. Irvine, J. C. S. 1904, **85**, 1056. T. Purdie and D. Paul, J. C. S. 1907, **91**, 296. H. Pottevin, Compt. rend. 1903, **136**, 170. E. Fischer, Ber. 1914, **47**, 1980. E. Armstrong, "Monographs on Biochemistry," The Simple Carbohydrates and the Glucosides, 1913, 49. J. Irvine, A. Fyfe and T. Hogg, J. C. S. 1915, **107**, 528. C. Hudson and D. Brauns, J. A. C. S. 1916, **38**, 1216. E. Fischer, Ber. 1893, **26**, 2440; J. C. S. 1907, **91**, 294. C. O'Sullivan and F. Tompson, J. C. S. 1890, **57**, 920.

4. J. C. S. 1919, **115**, 809; abst. C. A. 1919, **13**, 2856; J. S. C. I. 1919, **38**, 691-A; Bull. Soc. Chim. 1920, (4), **28**, 73; Chem. Zentr. 1920, **91**, I, 158.

5. Zts. Elektrochem. 1920, **26**, 232; abst. Paper, 1920, **27**, No. 13, 13; No. 26, 32; C. A. 1921, **15**, 1619; 1922, **16**, 2221; J. C. S. 1920, **118**, i, 532; J. C. S. Ann. Rep. 1920, **17**, 67; J. S. C. I. 1921, **30**, 1332.



ber of the ethyldextrin acetates produced should be less than that of the ethyldextrose.

J. Irvine, A. Fyfe and T. Hogg<sup>1</sup>, using a *v*-methylglucoside prepared according to the method of E. Fischer<sup>2</sup>, methylated under various described conditions, and obtained tetramethyl-*v*-methylglucoside, trimethyloxy-*v*-methylglucoside, tetramethylpentitol, tetramethylgluconlactone and tetramethylsorbitol.

In the preparation of molded articles from cellulose ethers, G. Leysieffer<sup>3</sup> presses and molds the ether by heat alone, or with the addition of a relatively small amount of benzene, the solvent being afterwards evaporated and the dry powder remaining pressed at 160°. The product is said to be especially applicable to the electrical insulation industry. To still further reduce the inflammability, calcium sulfate and triphenyl phosphate are added, either to cellulose ethers<sup>4</sup>, or to cellulose esters as acetylated cellulose.

During the period 1914-1920, there was issued to L. Lilienfeld a series of three basic patents. One process

1. J. C. S. 1915, **107**, 524; abst. C. A. 1915; **9**, 1907; J. S. C. I. 1915, **34**, 627; Chem. Zentr. 1915, **86**, II, 267; Meyer Jahr. Chem. 1915, **25**, 108.

2. Ber. 1914, **47**, 1980; abst. C. A. 1914, **8**, 3036; J. S. C. I. 1914, **33**, 770; Bull. Soc. Chim. 1915, (4), **18**, 136.

3. U. S. P. 1427690; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1922, **41**, 808-A; Kunst. 1925, **15**, 12; Chem. Zentr. 1922, **93**, IV, 1183. E. P. 156752; abst. J. S. C. I. 1921, **40**, 732-A; C. A. 1921, **15**, 1812; Chem. Zentr. 1921, **92**, II, 822. D. R. P. 343183; abst. Chem. Zentr. 1922, **93**, II, 101; Chem. Tech. Uebers. 1923, **47**, 172; Chim. et Ind. 1923, **9**, 354. F. P. 528399; abst. Chem. Zentr. 1922, **93**, II, 651. Swiss P. 91574; abst. Chem. Zentr. 1922, **93**, II, 1001; Kunst. 1923, **13**, 45. Aust. P. 89590; abst. Chem. Zentr. 1923, **94**, I, 1066.

4. E. P. 206770; abst. C. A. 1924, **18**, 1199; Kunst. 1925, **15**, 27; Ann. Rep. S. C. I. 1924, **9**, 147; Chem. Zentr. 1924, **95**, I, 981. F. P. 562667; abst. Chem. Zentr. 1924, I, 981; Kunst. 1924, **14**, 43. D. R. P. 396051; abst. Chem. Zentr. 1924, **95**, II, 2623; Kunst. 1925, **15**, 122.

covers the alkylation of starches<sup>1</sup>, a starch, for the purposes of the invention, covering all carbohydrates other than cellulose. These ethereal derivatives of the polyoses include etherified amylan, carrageen, mucilage, dextrans, cellulosin, lichenin, and geloses. The general methods of manufacture are as previously described by him, it having been found that the reaction proceeds in two stages. In the first stage, ethers soluble in water are obtained, and upon further etherification, ethers result which are water-insoluble. By the action of ethyl iodide or ethyl sulfate on starch in 10% NaOH solution, starch ethyl ethers (ethyl-starches) are obtained which are distinguished by their solubility in water. Another form is insoluble both in hot or cold water and forms a white powder. Tragacanth ethyl ether, similarly prepared, is a white or grey powder, insoluble in hot or cold water. Dextrin ethyl ether has similar properties. Inulin ethyl ether forms a viscid mass insoluble in water, hot or cold. The ethers are stable on heating and in the presence of acids and alkalis, their solutions in organic solvents leaving transparent films highly resistant to chemical and physical treatment.

Another process<sup>2</sup> is directed to the formation of highly-etherified celluloses, both alkyl, aralkyl and aryl, and in-

1. U. S. P. 1350820; abst. C. A. 1920, **14**, 3251; J. S. C. I. 1920, **39**, 654-A; Paper, 1921, **17**, No. 20, 19. E. P. 3370, 1914; abst. J. S. C. I. 1916, **35**, 534; Kunst. 1918, **8**, 42; J. Soc. Dyers, 1916, **32**, 181. F. P. 468162; abst. J. S. C. I. 1914, **33**, 958; Mon. Sci. 1916, **83**, 16. Chem. Ztg. 1914, **38**, 651; Chem. Ztg. Rep. 1915, **39**, 69. Aust. P. Appl. 1274, 1913; abst. Chem. Ztg. 1919, **43**, 649. Aust. P. 82866; abst. C. A. 1923, **17**, 1803; Chem. Ztg. 1920, **44**, 877; Chem. Zentr. 1921, **92**, IV, 41; J. C. S. 1921, **119**, 650. Ital. P. 140506; abst. Chem. Ztg. 1914, **38**, 1027. D. R. P. 360415; abst. Chem. Tech. Rep. 1922, **46**, 366; Chem. Zentr. 1923, **94**, II, 264. Aust. P. Appl. 2182, 1920; abst. Chem. Ztg. 1922, **46**, 687. Nor. P. 27507; abst. C. A. 1917, **11**, 1748. Can. P. 248226; abst. C. A. 1925, **19**, 3491.

2. U. S. P. 1483738; abst. C. A. 1924, **18**, 1198; J. S. C. I. 1924, **43**, 291-B. E. P. 149320; abst. C. A. 1921, **15**, 436; Chem. Met. Eng. 1920, **23**, 1269; Paper, 1921, **28**, 33; J. S. C. I. 1922, **41**, 53-A; Ann. Rep. S. C. I. 1921, **6**, 133, 138. F. P. 523931; abst. Chem. Zentr. 1921, **92**, IV, 1140-R. D. R. P. 475214; abst. C. A. 1929, **23**, 3232; Chem. Zentr. 1929, **100**, 237-R.

cluding the methyl-, ethyl- and benzyl-celluloses. They are preferably prepared from the lower alkylated cellulose ethers by further alkylation in the absence of water, or in the presence of only moderate amounts of water. For the further alkylation, a large excess of alkali is not required, and a quantity calculated on the amount of alkylating-agent present is sufficient; an excess of alkali may, however, be employed, in which case the amount of alkylating-agent required is less than that necessary when considerable quantities of water are present. The products obtained are distinguished by their resistance to cold water and by their solubility in a large number of volatile solvents. The lower alkylated ethers may first be isolated from the primary alkylating mixtures, as, for example, by precipitation with hot water, alcohol, alcohol-ether, or acetone; or the further alkylation may be carried out in the primary alkylating mixture after complete or partial removal of the excess of water; and if only a small excess of alkali is to be employed this may be incorporated in the mixture before the water is driven off, provided that care is taken as by the use of a low temperature, not to damage the ether. The removal of the water may be effected at atmospheric or reduced pressure, with or without heating, and it is facilitated by energetic stirring or kneading; depending on the proportion of water driven off, a paste or powdery mass is obtained. For the further alkylation, the finely-divided or pasty material is mixed if necessary with an additional quantity of alkali hydroxide, added at once or in small quantities; the alkylating-agent is added and the mixture heated, or it is added slowly with heating; the ether is separated by the addition of water, acidified if necessary, collected, washed with dilute acid and then with water, and dried. By-products such as alcohols or ethers may be distilled off during or after the alkylation, or may be recovered from the alkylating mixture either by steam distillation or by extraction with suitable solvents. In an example the preparation of an ethyl ether of cellulose is described in which

a viscose or an alkali- or hydro-cellulose and ethyl sulphate are the primary reacting materials.

The third process has to do with the preparation of plastic masses containing etherified celluloses, especially benzylcellulose, by combining them with certain tar oils<sup>1</sup>, the latter being prepared by the action of acetylene in the presence of aluminum chloride upon coal tar oil high-boiling fractions. In carrying out the process<sup>2</sup>, a cellulose ether dissolved in benzene, benzene and alcohol, chloroform, acetone or admixtures of them, is mixed with the tar oil, which in itself has a high dissolving power for the etherified celluloses, and the plastic mass formed, worked up in a manner analogous to the fabrication of celluloid. Detailed formulas are given for the manufacture of celluloid, artificial leather, and insulating material.

The J. Paiseau process for producing artificial pearls and other nacreous objects<sup>3</sup>, comprises coating an object, as a ball or button, with a cellulose ether solution to which has been incorporated dehydrated goldfish scales. A. Pel-

1. U. S. P. 1563204; abst. C. A. 1926, **20**, 503; J. S. C. I. 1926, **45**, 483-B; Chem. Zentr. 1926, **97**, I, 1709. E. P. 149317; abst. C. A. 1921, **15**, 434; Chem. Zentr. 1921, **92**, I, 52; J. S. C. I. 1921, **40**, 840-A; Rev. de Chim. Ind. 1921, **30**, 280. E. P. 149319; abst. C. A. 1921, **15**, 419; J. S. C. I. 1922, **41**, 95-A; Chem. Zentr. 1921, **92**, I, 44. F. P. 521000; abst. Chim. et Ind. 1922, **7**, 762; Chem. Zentr. 1921, **92**, IV, 826-R. D. R. P. 357707; abst. Chem. Zentr. 1922, **93**, IV, 964-R. Aust. P. 90010; abst. Kunst. 1923, **13**, 45; Chem. Zentr. 1923, **94**, II, 1066-R. Dan. P. 29621. Ital. P. 210/536. Nor. P. 37755. Swed. P. 54449. See his U. S. P. 1625416; E. P. 171661; F. P. 535132; D. R. P. 504226.

2. E. P. 149317; abst. C. A. 1921, **15**, 434; Chem. Zentr. 1921, **92**, I, 52; J. S. C. I. 1921, **40**, 840-A; Rev. de Chim. Ind. 1921, **30**, 280. F. P. 417392; abst. Mon. Sci. 1913, **88**, 45; C. A. 1913, **7**, 1987; Chem. Ztg. Rep. 1913, **37**, 98; J. S. C. I. 1911, **30**, 38; Kunst. 1911, **1**, 73; Rev. de Chim. Ind. 1910, **21**, 390. F. P. 16144 Addn. to F. P. 417392. Aust. P. 54719; abst. Kunst. 1912, **2**, 393.

3. U. S. P. 1438395; abst. Chem. Zentr. 1923, **94**, II, 934; C. A. 1923, **17**, 860. E. P. 23137, 1914; abst. J. S. C. I. 1919, **38**, 473-A. F. P. 473533. Belg. P. 293417, 313237, 320301. Cf. C. Paiseau-Feil, U. S. P. 978394, 1910. E. P. 22420, 1909; abst. C. A. 1911, **5**, 218. E. P. 23137, 1914; abst. J. S. C. I. 1919, **38**, 473-A. F. P. 407092, Addn. 12922, 13035, 18507, 19109. 19255, 1913; 416696, 420885, 1909; abst. C. A. 1912, **6**, 1989. D. R. P. 222248; abst. Wag. Jahr. 1910, **56**, II, 573. D. R. P. 215672, 233648; abst. C. A. 1910, **4**, 682; 1911, **5**, 2745.

lerin<sup>1</sup> has described a method for preparing hydrated cellulose especially suitable for cellulose ether formation, which involves utilizing the waste cellulose hydrate obtained from viscose rayon and cellophane sheet manufacture as the initial cellulosic material to be etherified. According to P. Seel<sup>2</sup> plastic compositions result of wide industrial applicability by combining cellulose ethers with chlorinated naphthalenes or anthracenes, as  $\alpha$ -monochloronaphthalene and tetrachloronaphthalene, the ether being first dissolved in alcohol and chloroform and the chlorinated body added in about the ratio of 10-20 parts to 50-100 parts cellulose ether.

S. Sheppard<sup>3</sup> has described a photographic element for color photography, in which a cellulose ether is utilized as the dye carrying medium. C. West<sup>4</sup> has summarized our published knowledge upon the alkyl ethers of starch, with special references to the L. Lilienfeld disclosures. A patent was granted for the use of esters of adipic acid as cellulose ether solvents and gelatinants, including the methyl and diethyl esters of adipic and *b*-methyladipic acids<sup>5</sup>.

**Technical Development, 1921-1925.** Notwithstanding the relative paucity of general scientific contributions during this semi-decade, primarily accountable for by the fact that scientists and technicians during the preceeding period of hostilities had devoted their intellectual energy more towards the warlike pursuits rather than to development in the peaceful arts, the growing interest in this subject and faith in its perpetuity and potentialities, is evidenced by the more than three hundred different investigations published

1. U. S. P. 1128624; abst. C. A. 1915, **9**, 1114; J. S. C. I. 1915, **34**, 349; Mon. Sci. 1915, **82**, 45; J. Soc. Dyers, 1915, **31**, 127.

2. U. S. P. 1281080; abst. C. A. 1919, **13**, 73; J. S. C. I. 1919, **38**, 8-A; Chim. et Ind. 1919, **2**, 831.

3. U. S. P. 1290794; abst. C. A. 1919, **13**, 818; J. S. C. I. 1919, **38**, 200-A; Chim. et Ind. 1919, **2**, 1355.

4. Paper, 1920, **27**, 16, 36. Translation of article by Wedorf, Kunst. 1920, **10**, 112; abst. C. A. 1920, **14**, 2551; Chim. et Ind. 1921, **5**, 332; Caout. Gutta. 1920, **17**, 10672; Chem. Zentr. 1920, **91**, IV, 753.

5. D. R. P. 317412; abst. J. S. C. I. 1920, **39**, 361-A.

and inventions granted in the cellulose ether art during this five-year period, as indicated herein.

A. Backhaus<sup>1</sup> has described a method of making plastic compositions in which nitro-, acetyl-, methyl-, or ethyl-cellulose is combined with methyl-, ethyl-, methylethyl-, propyl- or butyl-acetoacetate in conjunction with a volatile solvent. P. Balke and G. Leysieffer<sup>2</sup> have described the preparation of a phonograph record, said to be of superior quality and durability, comprising combining ethylcellulose with filling material and an excess of methylurea or ethylurea as a gelatinizing agent, and have patented the mixture<sup>3</sup> as especially desirable for the production of toilet articles<sup>4</sup>.

The Bemberg A. G.<sup>5</sup> in the production of ethylcellulose artificial filaments, coagulate the latter by water at a low temperature to such an extent that solidification of the filaments is incomplete (i.e., the core is still plastic), the setting of the filaments being completed by immersion in water at a higher temperature. By operating in this manner, it is claimed that the formation of deposits on the walls of the spinning apparatus is obviated. E. Berl combines cellulose esters with cellulose ethers<sup>6</sup>, because denitrated nitrocellulose or acetylcellulose is weak in the wetted state and the cellulose ethers dye with difficulty. By combining ethylcellulose with nitrocellulose, or acetylcellulose with benzylcellulose, it is claimed that improved resistance to dry and wet

1. U. S. P. 1437952; abst. *Caout. et Gutta.* 1923, **20**, 11931; *C. A.* 1923, **17**, 879; *J. S. C. I.* 1923, **42**, 91-A; *Kunst.* 1925, **15**, 43; *Chem. Zentr.* 1923, **94**, II, 1123.

2. U. S. P. 1456047; abst. *C. A.* 1923, **17**, 2482. *E. P.* 169232; abst. *C. A.* 1922, **16**, 803. *E. P.* 170568, Addn. to *E. P.* 169232.

3. *E. P.* 181697; abst. *C. A.* 1923, **17**, 209; *Chem. Zentr.* 1922, **93**, IV, 850; *Kunst.* 1924, **14**, 90; *Caout. et Gutta.* 1923, **20**, 11687. *Belg. P.* 291528, 303245, 303246. *Swiss P.* 91157; abst. *Kunst.* 1923, **13**, 45; *Chem. Zentr.* 1922, **93**, II, 885-R. *Swiss P.* 115322, Addn. to *Swiss P.* 91157; abst. *Chem. Zentr.* 1926, **97**, II, 2851.

4. P. Balke and G. Leysieffer, *E. P.* 181696; *Caout. et Gutta.* 1923, **20**, 11687. *E. P.* 181697, 229674; abst. *C. A.* 1925, **19**, 3174; *J. S. C. I.* 1926, **45**, 268-B. Cites *E. P.* 154157; abst. *J. S. C. I.* 1922, **41**, 383-A.

5. *E. P.* 244492; abst. *Chem. Zentr.* 1926, **97**, II, 2266.

6. U. S. P. 1484004; abst. *C. A.* 1924, **18**, 1198; *J. S. C. I.* 1924, **43**, 415; *Kunst.* 1925, **15**, 163. *D. R. P.* 385962; abst. *Chem. Zentr.* 1924, **95**, I, 1127.

strength is obtained, and better dyeing properties. He claims<sup>1</sup> that cellulose ether filaments are best prepared in the stretch-spinning method by first dissolving the ether, then flocculating with aqueous solutions of such salts as calcium or ammonium nitrates, ammonium sulfate or sodium formate, acetate, oxalate or chloride. In a specific example, a dilute solution of acetyl- and methyl-cellulose in methylethyl ketone is first passed into a mixture of acetone and water, then into a mixture of calcium or ammonium nitrate which contains methylethyl ketone, and then into the pure salt solution free from ketone.

J. Briggs and W. Yorke<sup>2</sup> have described an apparatus for the manufacture of cellulose ether filaments by the evaporative spinning method, and involving mechanical details for solvent recovery after filament formation. C. Palmer and W. Whitehead<sup>3</sup> have devised a process and apparatus for artificial filament production from methyl-, ethyl- and benzyl-cellulose, and involving the winding and twisting of the filaments as a simple and economical single operation. Where the spinning operation is conducted in volatile solvents and downwards through a hollow casing in a current of warm air to remove solvent, the finished thread is passed through a small hole in the side of the casing, and wound up by apparatus placed outside the casing, a travel of 2-3 seconds in a current of air at 30-35°, being sufficient to efficiently remove the solvent<sup>4</sup>. Or<sup>5</sup>, as an aid in winding, twisting, etc., vegetable or animal oils, fats or waxes may be added to the filament as lubricants, thus preventing or minimizing the tendency to hair-

1. U. S. P. 1679850; abst. J. S. C. I. 1928, **47**, 744-B. E. P. 230813; abst. J. S. C. I. 1925, **44**, 877-B; Ann. Rep. S. C. I. 1925, **10**, 154; Chem. Zentr. 1925, **96**, II, 369. Belg. P. 306174.

2. U. S. P. 1541104; abst. C. A. 1925, **19**, 2276. E. P. 203092.

3. E. P. 198023; abst. J. S. C. I. 1923, **42**, 765-A.

4. British Cellulose & Chemical Mfr. Co., Ltd., and H. Roy, E. P. 165519; abst. C. A. 1922, **16**, 837; J. S. C. I. 1921, **40**, 577-A; Chem. Zentr. 1922, **93**, I, 1229. U. S. P. 1602125.

5. British Cellulose & Chemical Mfr. Co., Ltd., and C. Ryley, C. Palmer and S. Welch, E. P. 215417; abst. C. A. 1924, **18**, 2967; Faser, 1924, **6**, 130; Chem. Zentr. 1924, **95**, II, 1534.

ing or fluffing or electrification in the threads manufacture and subsequent treatments.

K. Bratring<sup>1</sup> in the production of photographic films, secures a supporting layer of cellulose hydrate to the gelatin side of a film after it has passed through all the baths. The base may comprise a cellulose ether. In the purification of cellulose ethers<sup>2</sup> the excess of caustic soda after the alkylation process, is neutralized with an aqueous solution of sulfurous acid.

In 1924, a series of 41 United States patents issued to S. Carroll and assigned to the Eastman Kodak Co., covering the use of various cellulose ether solvents and plasti-fying bodies. The solvents embraced in these patents may be classified as follows: Let "A" represent one or more monohydroxyaliphatic alcohols of less than 6 carbon atoms (methyl, ethyl, *n*-propyl, isopropyl, *nor*-butyl, *sec*-butyl, amyl), and "B" the corresponding acetate. The solvents of the Carrol patents then embrace, a mixture of A and/or B with methyl acetone (a commercial mixture of methyl alcohol, acetone and methyl acetate)<sup>3</sup>, butyl tartrate<sup>4</sup>, benzaldehyde<sup>5</sup>, cyclohexanone<sup>6</sup>, cyclohexanol<sup>7</sup>, methylene chloride<sup>8</sup>, ethylene trichloride<sup>9</sup>, ethylene bromide<sup>10</sup>, ethyl

1. E. P. 307431. D. R. P. 357010; abst. J. S. C. I. 1922, **41**, 917-A; Chem. Zentr. 1922, **93**, II, 816; Phot. Abst. 1923, **3**, 15.

2. R. Baybutt, U. S. P. 1510735; abst. C. A. 1924, **18**, 3719; J. S. C. I. 1925, **44**, 7-B; Chem. Zentr. 1925, **96**, I, 799.

3. U. S. P. 1500366; abst. C. A. 1924, **18**, 2810; J. S. C. I. 1924, **43**, 742-B.

4. U. S. P. 1467103; abst. C. A. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.

5. U. S. P. 1467104; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.

6. U. S. P. 1467101; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.

7. U. S. P. 1467097; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A. U. S. P. 1467098; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A. Acetophenone (U. S. P. 1467098; abst. J. S. C. I. 1923, **42**, 1065-A) is also included.

8. U. S. P. 1467102; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.

9. U. S. P. 1467105; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.

10. U. S. P. 1467100; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.



iodide<sup>1</sup>, dibenzylamine<sup>2</sup>, ethylbenzene<sup>3</sup>, dimethylaniline<sup>4</sup>, and diphenylmethane<sup>5</sup>. An admixture of A with perchlorethylene<sup>6</sup>, pentachlorethane<sup>7</sup>, furfural<sup>8</sup>, phenol<sup>9</sup>, xylene<sup>10</sup>, methyl salicylate<sup>11</sup>, phenyl propyl alcohol<sup>12</sup>, monochlorbenzene<sup>13</sup>, monochloronaphthalene<sup>14</sup>, ethylbenzylamine<sup>15</sup> methyl benzoate<sup>16</sup>, and resorcinol diacetate<sup>17</sup>. Ethylene chloride is combined either with A<sup>18</sup>, or with B<sup>19</sup>. A phenyl ether group (combined with A<sup>20</sup>, and including phenetole (phenylethyl ether), anisole (phenylmethyl ether), *nor*-butyl-*o*-cresyl ether, benzylethyl ether, diphenyl

1. U. S. P. 1467099; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.
2. U. S. P. 1467092; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.
3. U. S. P. 1467093; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.
4. U. S. P. 1467094; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.
5. U. S. P. 1467095; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.
6. U. S. P. 1450714; abst. C. A. 1923, **17**, 1887; J. S. C. I. 1923, **42**, 494-A; Caout. et Gutta. 1924, **21**, 12092.
7. U. S. P. 1434427; abst. J. S. C. I. 1923, **42**, 50-A; Caout. et Gutta. 1923, **20**, 11931.
8. U. S. P. 1450716; abst. C. A. 1923, **17**, 1887; J. S. C. I. 1923, **42**, 494-A; Caout. et Gutta. 1924, **21**, 12092.
9. U. S. P. 1434426; abst. C. A. 1923, **17**, 467; Caout. et Gutta. 1923, **20**, 11931.
10. U. S. P. 1431905; abst. C. A. 1922, **16**, 4346; J. S. C. I. 1922, **41**, 894-A.
11. U. S. P. 1450715; abst. C. A. 1923, **17**, 1887; J. S. C. I. 1923, **42**, 494-A; Caout. et Gutta. 1924, **21**, 12092.
12. U. S. P. 1444351; abst. C. A. 1923, **17**, 1329; Chem. Met. Eng. 1923, **28**, 510; J. S. C. I. 1923, **42**, 305-A.
13. U. S. P. 1411708; abst. C. A. 1922, **16**, 1915; J. S. C. I. 1922, **41**, 267-A.
14. U. S. P. 1437792; abst. C. A. 1923, **17**, 878; Caout. et Gutta. 1923, **20**, 11931.
15. U. S. P. 1467096; abst. Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.
16. U. S. P. 1469813; abst. C. A. 1923, **17**, 3919; J. S. C. I. 1923, **42**, 1172-A; Kunst. 1924, **14**, 44.
17. U. S. P. 1552792; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Caout. et Gutta. 1926, **23**, 13316.
18. U. S. P. 1429188; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1922, **41**, 807-A.
19. U. S. P. 1464170; abst. J. S. C. I. 1923, **42**, 1065-A; Kunst. 1924, **14**, 44.
20. U. S. P. 1479955; abst. C. A. 1924, **18**, 904; J. S. C. I. 1924, **43**, 213; Kunst. 1925, **15**, 83.

ether, *nor*-butylphenyl ether, *nor*-butylbenzyl ether and methyl-*o*-cresyl ether. Combinations of the lower aliphatic ketones with A<sup>2</sup> include methylethyl, methylpropyl, methylbutyl, methylamyl, diethyl, dipropyl, diisopropyl, dibutyl, diamyl ketones. Or, combinations of resorcinol<sup>3</sup> or ethylacetanilid<sup>4</sup> with methyl alcohol or methyl acetate. Chloroform combined with methyl alcohol<sup>5</sup>, or with a mixture of methyl alcohol and ethyl acetate<sup>6</sup>, or chloroform and ethyl acetate<sup>7</sup>. Other admixtures of solvents coming within patent protection granted to Carroll are a mixture of methyl alcohol 50-25, with toluene 50-75<sup>8</sup>; methyl acetate in conjunction with monochloronaphthalin<sup>9</sup>, and ethyl acetate 92, ethyl alcohol 7 and 1 part of water<sup>10</sup>.

In combination with a volatile solvent composed of ethyl alcohol and benzene, there has also been patented the use as cellulose ether dissolving compositions, ethyl or phenyl phthalates<sup>11</sup>, *n*-, or *iso*-butyl or amyl benzoates<sup>12</sup> or salicylates<sup>13</sup>, or a flowable composition comprising pentaerythritol tetracetate in a volatile solvent composition<sup>14</sup>. He

2. U. S. P. 1469812; abst. C. A. 1923, **17**, 3919; J. S. C. I. 1923, **42**, 1172-A; Faser. 1924, **6**, 11.

3. U. S. P. 1552793; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Caout. et Gutta. 1926, **23**, 13316; Chem. Zentr. 1926, **I**, **97**, 541.

4. U. S. P. 1552794; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Caout. et Gutta. 1926, **23**, 13316; Chem. Zentr. 1926, **I**, **97**, 541.

5. U. S. P. 1405487; abst. C. A. 1922, **16**, 1316; J. S. C. I. 1922, **41**, 213-A; Caout. et Gutta. 1922, **19**, 11653.

6. U. S. P. 1431906; abst. C. A. 1922, **16**, 4346; J. S. C. I. 1922, **41**, 894-A; Kunst. 1924, **14**, 91.

7. U. S. P. 1464169; abst. C. A. 1923, **17**, 3253; J. S. C. I. 1923, **42**, 1065-A.

8. U. S. P. 1441143; abst. C. A. 1923, **17**, 938; Chem. Met. Eng. 1923, **28**, 271; J. S. C. I. 1923, **42**, 180-A; Kunst. 1923, **13**, 92.

9. U. S. P. 1467091; abst. C. A. 1923, **17**, 3789; Chem. Met. Eng. 1923, **29**, 679; J. S. C. I. 1923, **42**, 1065-A.

10. U. S. P. 1425173; abst. C. A. 1922, **16**, 3393; J. S. C. I. 1922, **41**, 748-A.

11. H. Clarke, U. S. P. 1405491; abst. C. A. 1922, **16**, 1316; J. S. C. I. 1922, **41**, 248-A.

12. H. Clarke, U. S. P. 1405490; abst. C. A. 1922, **16**, 1316; J. S. C. I. 1922, **41**, 248-A; Caout. Gutta. 1922, **19**, 11653.

13. H. Clarke, U. S. P. 1395905; abst. C. A. 1922, **16**, 646; J. S. C. I. 1921, **40**, 886-A.

14. H. Clarke. U. S. P. 1548933; abst. C. A. 1925, **19**, 3018:

has also described a photographic film and compound support<sup>1</sup> made up of a nitrocellulose layer surrounded by a cellulose ether layer, upon which is spread the photographically sensitive stratum, the compound support comprising a pyroxylin layer coated on each face with a lacquer composed of ethylcellulose 100, benzene 340 and ethyl alcohol 170. L. Clement and C. Riviere<sup>2</sup> have pointed out that the viscosity of solutions of the cellulose ethers varies with the degree of modification of the cellulose used for etherification, an unmodified cellulose giving a higher viscosity. Also, that addition of ethyl alcohol to the solvent diminishes in general, the viscosity of the solution.

A series of cellulose ether patents has been granted J. Donohue which may be said to be complementary to the S. Carroll patents above indicated. Assuming the letter A represents, as before, either methyl, ethyl, propyl, butyl, or amyl alcohols, these patents cover the use of the following as solvent combinations, especially for the water-insoluble ethylcelluloses. "A" in conjunction with methyl, ethyl, propyl, butyl or amyl propionates<sup>3</sup>; epichlorhydrin<sup>4</sup>; ethyl succinate<sup>5</sup>; ethyl lactate<sup>6</sup>; acetylacetone<sup>7</sup>, hexyl acetate<sup>8</sup>; carvone<sup>9</sup>; monobrom- or dibrom-benzene or

1. S. Carroll, U. S. P. 1441142; abst. C. A. 1923, **17**, 938; J. S. C. I. 1923, **42**, 203-A.

2. Rev. gen. Colloides, 1924, **2**, No. 3, 11; abst. C. A. 1924, **18**, 3714; Chem. Zentr. 1924, II, 24.

3. U. S. P. 1473217; abst. C. A. 1924, **18**, 469; J. S. C. I. 1924, **43**, 12; Chem. Zentr. 1924, **95**, I, 525; Kunst. 1925, **15**, 43.

4. U. S. P. 1473218; abst. C. A. 1924, **18**, 469; J. S. C. I. 1924, **43**, 12; Chem. Zentr. 1924, **95**, 525; Kunst. 1925, **15**, 43.

5. U. S. P. 1473219; abst. J. S. C. I. 1924, **43**, 12; Chem. Zentr. 1924, **95**, I, 525; Kunst. 1925, **15**, 43.

6. U. S. P. 1552796; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, **97**, I, 540; Caout. et Gutta. 1926, **23**, 13316.

7. U. S. P. 1552800; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, **97**, I, 795; Caout. et Gutta. 1926, **23**, 13316.

8. U. S. P. 1552801; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, **97**, I, 795; Caout. et Gutta. 1926, **23**, 13316.

9. U. S. P. 1552802; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. Soc. Chem. Ind. 1926, **11**, 618; Chem. Zentr. 1926, **97**, I, 795.

-toluene<sup>1</sup>; methyl, ethyl, propyl, butyl, amyl formates<sup>2</sup> or carbonates<sup>3</sup>; propyl, butyl or amyl butyrates<sup>4</sup>; aliphatic halid toluene derivatives (benzyl chloride, benzal chloride, benzotrichloride, benzyl bromide, benzal bromide<sup>5</sup>, benzotribromide); methylacetanilid, acetyl-*p*-phenetidine, diethyl carbanilid, aniline acetate, phenyl urea, diphenylethylene diamine, benzanilid, *p*-dimethylaminobenzanilid, *p*-dimethylaminophenyl acetate<sup>6</sup>; polyhydroxybenzene acetates (monacetate and diacetate of pyrogallol, resorcinol, catechol, hydroxyquinol, hydroquinone<sup>7</sup>. Compound solvent combinations have been specified and claimed, as mixtures of chloroform and ethyl alcohol<sup>8</sup>; benzene and carbon tetrachloride<sup>9</sup>; acetone and benzene<sup>10</sup>.

1. U. S. P. 1552799; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, **97**, I, 795; Caout. et Gutta. 1926, **23**, 13316.

2. U. S. P. 1552806; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, **97**, I, 796; Caout. et Gutta. 1926, **23**, 13316.

3. U. S. P. 1552805; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Chem. Zentr. 1926, **97**, I, 796; Caout. et Gutta. 1926, **23**, 13316; Ann. Rep. S. C. I. 1926, **11**, 618.

4. U. S. P. 1552804; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, **97**, I, 796; Caout. et Gutta. 1926, **23**, 13316.

5. U. S. P. 1552798; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Chem. Zentr. 1926, **97**, I, 540; Caout. et Gutta. 1926, **23**, 13316; Ann. Rep. S. C. I. 1926, **11**, 618.

6. U. S. P. 1460097; abst. C. A. 1923, **17**, 2957; J. S. C. I. 1923, **42**, 925-A; Ann. Rep. S. C. I. 1923, **8**, 151; Kunst. 1925, **15**, 43; Faser. 1924, **6**, 11; Chem. Zentr. 1924, **95**, I, 267.

7. U. S. P. 1552803; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, **97**, I, 795, 796; Caout. et Gutta. 1926, **23**, 13316.

8. U. S. P. 1394505; abst. C. A. 1922, **16**, 494; J. S. C. I. 1921, **40**, 886-A; Phot. Abst. 1922, **2**, 14, 15, 138; Chem. Zentr. 1922, **93**, II, 219.

9. U. S. P. 1434432; abst. C. A. 1923, **17**, 467; J. S. C. I. 1923, **42**, 50-A; Chem. Zentr. 1923, **94**, I, 643; Caout. et Gutta. 1923, **20**, 11931; Kunst. 1924, **14**, 91.

10. U. S. P. 1552797; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 915-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, **97**, I, 540; Caout. et Gutta. 1926, **23**, 13316.

In the J. Donohue method of cellulose ether manufacture<sup>1</sup>, the main feature is the use of a centrifugal to remove excess of water from the alkali-cellulose, dry powdered sodium hydroxide being added, after which the mass is charged into an autoclave and etherified with ethyl chloride. In the production of cellulose ethers which yield transparent films free from haziness<sup>2</sup>, Donohue carries out the etherification in the presence of surfaces of nickel or alloys containing large amounts of nickel, as Monel metal. The film of Donohue is the antithesis of that of Carroll, the former preparing a photographic film by attaching to each side of the ether film, a coating either of cellulose acetate or nitrocellulose<sup>3</sup>.

An alcohol-soluble ethylcellulose and an alcohol-insoluble cellulose acetate are given as illustrative products. In an improvement on this idea<sup>4</sup>, a base which is slightly soluble in the solvent used in the preparation of the solution of the cellulose derivative from which the film is made, is used. Or the cellulose ether may be applied in the same manner as above outlined, using a traveling band or cardboard, sheet metal, linoleum, rubberized material or cellulose acetate<sup>5</sup>.

1. U. S. P. 1415023; abst. C. A. 1922, **16**, 2406; J. S. C. I. 1922, **41**, 542-A; Chem. Zentr. 1922, **93**, IV, 600; Chem. Tech. Uebers. 1922, **46**, 282; Caout. et Gutta. 1923, **20**, 11930.

2. U. S. P. 1489315; abst. C. A. 1924, **18**, 1908; J. S. C. I. 1924, **43**, 464-B; Chem. Zentr. 1924, **95**, II, 1992.

3. U. S. P. 1518396; abst. C. A. 1925, **19**, 576; Ann. Rep. S. C. I. 1925, **10**, 573; Chem. Zentr. 1925, **96**, I, 1148.

4. Cellon-Werke, A. Eichengruen; E. P. 224848, Addn. to E. P. 202306; abst. C. A. 1925, **19**, 1948; Kunst. 1925, **15**, 101; Chem. Zentr. 1925, **96**, I, 1665. D. R. P. 469317; abst. C. A. 1929, **23**, 1266; Chem. Zentr. 1929, **100**, I, 592.

5. Cellon-Werke, A. Eichengruen, E. P. 241590; abst. C. A. 1926, **20**, 3567; J. S. C. I. 1927, **46**, I, 165.

J. Chowdhury<sup>1</sup> has obtained polysaccharide ethers with hydroxy acids, by the action of chloroacetic acid on polysaccharides in the presence of concentrated aqueous sodium hydroxide, ethers are obtained which, when thoroughly dried, are insoluble in water and in organic solvents. In the case of the cellulose ethers of glycollic acid the preparation with the lowest content of acid had one molecular proportion of the latter to three glucose residues, whilst that with the highest acid content had three molecules in each glucose residue. By the action of phosphorus tri-iodide and water on the cellulose glycollic acid ethers, cellulose and glycollic acid were obtained. In the cases of starch and inulin the highest degrees of substitution attained were respectively 2 mols. and  $2\frac{1}{2}$  mols. of acid per glucose residue. The more highly substituted derivatives form insoluble salts with the alkaline-earth metals, and may be separated from the less highly substituted compounds of which the corresponding salts are soluble in water. The monosubstituted cellulose derivative exists as a lactone, that of starch as a mixture of free acid and lactone. The partly substituted cellulose derivatives may be methylated by means of methyl sulphate and sodium hydroxide, the carboxyl groups of the acid residues undergoing a partial methylation. The resulting product is soluble in cold, but insoluble in hot water. In the case of starch the carboxyl group does not undergo esterification and the product, which is soluble in both cold and hot water, shows a combined acid and methoxyl content corresponding with a substitution of  $2\frac{1}{3}$  of the three available hydroxyl groups in each glucose residue. By the action of chloropropionic acid and sodium hydroxide on cellulose, lactic acid ethers were obtained in small yields, but the formation of similar products was not observed using chloro- and bromo-malonic acids.

1. Biochem. Zts. 1924, **148**, 76; abst. C. A. 1925, **19**, 640; J. C. S. 1924, **126**, i, 1029; Chem. Zentr. 1924, **95**, II, 622. See D. R. P. 332203; abst. Chem. Zentr. 1921, **93**, II, 672.

He found that by 12 hours action of monochloroacetic acid on cellulose, starch or inulin in 40% NaOH, water-soluble esters of glycolic acid were prepared from 1 molecule polysaccharide to 12 molecules NaOH and 9 molecules  $\text{ClCH}_2\text{CO}_2\text{H}$ . The product was purified by extraction with EtOH and precipitation of the aqueous solution with EtOH. By repeated treatment with  $\text{ClCH}_2\text{CO}_2\text{H}$  the maximum amounts of acid which could be introduced were: in the case of cellulose, 3 molecules, starch, 2 molecules, inulin, 2.5 molecules to 1 glucose molecule. The alkaline earth salts of the esters containing the least acid were most soluble in water, and they were thus separated from those containing more acid. Various salts of these esters were prepared. The esters occurred partially in the lactone form in some instances. By treatment of the esters with  $\text{Me}_2\text{SO}_4$ , mixed esters were formed. In the case of cellulose not only OH, but also  $\text{CO}_2\text{H}$  groups, were methylated; in the case of starch, the latter were not methylated. By the action of  $\text{Cl}(\text{CH}_2)_2\text{CO}_2\text{H}$ , and of  $\text{ClCH}(\text{CO}_2\text{H})_2$  on cellulose, the corresponding esters were prepared in small yield.

G. Davidson<sup>1</sup> has evolved a series of cellulose ester and cellulose ether solvents, being alkyl ethers of mono- and poly-glycols, and including methyl-, ethyl-, *iso*-propyl-, *n*-propyl-, *iso*-butyl-, *n*-butyl-, and *iso*-amyl-propylene glycol; diethylpropylene glycol; monoethyl- and monophenyl-dipropylene glycol. A. DeWaele produces stencils for manuscript duplication<sup>2</sup>, by coating Yoshino paper with water-soluble ethers of cellulose and starch in conjunction with a tempering agent to render the film sufficiently sensitive to be cut by a stylus or in a typewriter.

C. Dreyfus has patented a method for pressed or moulded articles containing a cellulose ether or ester in com-

1. E. P. 255406; abst. C. A. 1927, **21**, 2798; J. S. C. I. 1927, **46**, 428; Chem. Zentr. 1927, **98**, I, 381. Belg. P. 325254. Can. P. 260463, 260464, 260465, 260466, 268571; abst. C. A. 1926, **20**, 3567; 1927, **21**, 2384, 2798.

2. E. P. 216648; abst. C. A. 1925, **19**, 178; J. S. C. I. 1924, **43**, 708-B.

bination with various resins<sup>1</sup>, of which rosin<sup>2</sup> is claimed as giving especially satisfactory results in the manufacture of such plastics as phonograph records. Acaroid resins (gum accroides, red gum, xanthorrhoea resin) are advocated as being particularly useful when combined with cellulose ethers or esters for airplane dopes<sup>3</sup>.

The inventions of H. Dreyfus in this five year period include activities in nearly the whole then known field of cellulose ether technics. In the manufacture of aryl or aralkyl cellulose ethers, as benzyl-, methyl-benzyl, phenylethyl-, chlorethylbenzyl-cellulose, the cellulose is first impregnated with about 4 molecular equivalents of NaOH in 50% solution, in the presence of a contact material as copper or copper salts, kneaded with 2-3 molecules of benzyl chloride or other etherifying body at 50-100° for 2 hours, additional NaOH and etherifier being added. The product is then precipitated in a large bulk of water and washed free from reactants. Or<sup>4</sup>, in the production of aralkyl ethers (say), methylbenzylcellulose, the cellulose is first partially etherified in the usual manner with methyl sulfate, then with benzyl chloride, or the partial benzylation may precede the methylation. As an excellent benzylcellulose solvent, also applicable to the methyl- and ethyl-celluloses, chloretone (chlorbutanol, dimethylcarbinolchloroform, trichlor-*ter*-butyl alcohol, methaform, acetone-chloroform, 1.1.1-trichlor-2-methylpropanol-2) has been put forth<sup>5</sup>, an example being ethyl- or benzyl-cellulose 70, chloretone 30, kneaded together in the usual way for making celluloid.

1. E. P. 215823; abst. C. A. 1924, **18**, 3458; Kunst. 1925, **15**, 144. See E. P. 132283, 133353, 154334, 174660, 179208.

2. E. P. 222167. Ital. P. 209183.

3. C. Dreyfus, E. P. 222168; abst. C. A. 1925, **19**, 1061; J. S. C. I. 1924, **43**, 977; Ann. Rep. S. C. I. 1924, **9**, 352. U. S. P. 1742587.

4. H. Dreyfus, E. P. 164375; abst. C. A. 1922, **16**, 495; J. S. C. I. 1921, **40**, 540-A; Ann. Rep. S. C. I. 1921, **6**, 138; Chim. et Ind. 1922, **8**, 654; Chem. Tech. Uebers. 1921, **45**, 327. U. S. P. 1451330; abst. C. A. 1923, **17**, 2505; J. S. C. I. 1923, **42**, 447-A; Chem. Zentr. 1924, I, 2759. F. P. 530891; abst. Chem. Zentr. 1922, II, 899-R. F. P. Addn. 24082 to F. P. 530891. Australian P. 2543, 1921.

5. E. P. 205195; abst. C. A. 1924, **18**, 1199; J. S. C. I. 1923, **42**, 1172-A; Chem. Zentr. 1924, I, 716; Kunst. 1924, **14**, 91.



In another method of cellulose etherification<sup>1</sup>, dry cellulose, of a type not soluble in alkali, is ground with alkali in benzene, toluene, carbon tetrachloride, ether or ligroin, the etherifying agent being added in the presence of the non-solvent diluents, or after their partial removal. The object of introduction of the liquids is to keep down the temperature during grinding of cellulose with alkali, and diminish the degradation of the cellulose. The essence of another H. Dreyfus cellulose etherification process<sup>2</sup>, is in connection with the ratio of water to alkali to cellulose, the total quantity of water employed—whether as water, moisture or solution, and whether introduced before or during the etherification, but disregarding water formed in the process itself, is restricted between the limits 0-100%, and preferably between zero and 25-50%, relative to the weight of the cellulose or conversion products. This rather involved sentence enunciates a principle evolved by Dreyfus, which has been the basis of broad litigation. In a modification of this process<sup>3</sup>, the total water in the reaction is restricted to a maximum of 1.5 times the weight of original cellulose used.

As plastic-inducing bodies of high boiling point and unusually low volatility are the alkylated sulfonamide derivatives<sup>4</sup>, the better known members being benzene monomethyl-, benzene methylethyl-, toluene-dimethyl-, toluene

1. E. P. 176420; abst. J. S. C. I. 1922, **41**, 324-A; Chim. et Ind. 1923, **9**, 769; Caout. & Gutta Percha, 1922, **19**, 11496; Chem. Zentr. 1922, IV, 182; Faserstoffe, 1923, **5**, 71. U. S. P. 1501207; abst. C. A. 1924, **18**, 2809; J. S. C. I. 1924, **43**, 743.

2. U. S. P. 1542541; abst. C. A. 1925, **19**, 2411; J. S. C. I. 1925, **44**, 587-B. E. P. 187639; abst. C. A. 1923, **17**, 1141; J. S. C. I. 1923, **42**, 10-A; Chem. Met. Eng. 1923, **28**, 511; Chem. Zentr. 1923, II, 643; Ann. Rep. S. C. I. 1923, **8**, 150; Chim. et Ind. 1923, **10**, 542. Can. P. 237709; abst. C. A. 1924, **18**, 1051. F. P. 549880. Australia P. 6250, Addn. to 2543.

3. Can. P. 236956; abst. C. A. 1924, **18**, 752.

4. E. P. 132283; abst. C. A. 1920, **14**, 346; J. S. C. I. 1919, **38**, 896-A; Chim. et Ind. 1920, **4**, 798; Kunst. 1920, **10**, 79; 1921, **11**, 61; 1923, **13**, 7. E. P. 133353; abst. J. S. C. I. 1920, **39**, 14-A; Chim. et Ind. 1921, **6**, 512; Kunst. 1920, **10**, 80, 198; 1923, **13**, 7. E. P. 154334; abst. C. A. 1921, **15**, 1075; J. S. C. I. 1921, **40**, 42-A; J. Soc. Dyers Col. 1921, **37**, 56; Chem. Zentr. 1921, II, 575.

methylethyl-, toluenedimethyl-, toluenediethyl-, xylene-methyl-, xylenethyl-, xylenedimethyl-, and xylenediethyl-sulfonamide. These thermoplasticizers have been patented for use in the nitrocellulose industry<sup>1</sup>, with cellulose ethers in general<sup>2</sup>, with methyl- or ethyl-cellulose<sup>3</sup>, or with benzyl- or ethylbenzyl-cellulose<sup>4</sup>.

A new class of etherified celluloses was applied for by H. Dreyfus on May 13, 1920<sup>5</sup>, a class of bodies obtained by the action upon cellulose or its conversion products with halogen derivatives of glycols or polyhydric alcohols or their ethers in presence of alkali solutions of high concentration, whereby the residue introduced into the cellulose molecule contains one or more hydroxyl groups. These halogen derivatives (such as ethylenechlor-hydrin, propylene chlorhydrin, glyceryl monochlorhydrin, glyceryl dichlorhydrin, epichlorhydrin) may be used in conjunction with the halogen derivatives of alkyl, benzyl or homologous groups. Reinforced sheets, webs or plates may be formed by combining methyl-, ethyl- or benzyl-cellulose in solution with camphor or camphor substitute, the solution being flowed into open-mesh metallic or other base<sup>6</sup>. Or, the cellulose ethers may be cast or molded into various products

1. U. S. P. 1454961; abst. C. A. 1923, **17**, 2362; J. S. C. I. 1923, **42**, 600-A; Chem. Zentr. 1923, IV, 1018; Kunst. 1924, **14**, 43.

2. E. P. 164384; abst. C. A. 1922, **16**, 494; J. S. C. I. 1921, **40**, 540-A; Ann. Rep. S. C. I. 1921, **6**, 139; Chim. et Ind. 1922, **8**, 1081; Chem. Zentr. 1921, IV, 883.

3. E. P. 164386; abst. C. A. 1922, **16**, 494; J. S. C. I. 1921, **40**, 540-A; Chem. Met. Eng. 1921, **25**, 715; Ann. Rep. S. C. I. 1921, **6**, 139; Chim. et Ind. 1922, **8**, 1081; Chem. Zentr. 1921, IV, 883. U. S. P. 1454959; abst. C. A. 1923, **17**, 2362; J. S. C. I. 1923, **42**, 600-A; Chem. Zentr. 1923, IV, 1018.

4. E. P. 164385; abst. J. S. C. I. 1921, **40**, 540-A; Ann. Rep. S. C. I. 1921, **6**, 139; Chim. et Ind. 1922, **8**, 1081; Chem. Zentr. 1921, IV, 883. U. S. P. 1454960; abst. C. A. 1923, **17**, 2362; J. S. C. I. 1923, **42**, 600-A; Chem. Zentr. 1923, IV, 1018.

5. E. P. 166767; abst. C. A. 1922, **16**, 830; J. S. C. I. 1921, **40**, 654-A; Chem. Met. Eng. 1921, **25**, 1021; Ann. Rep. S. C. I. 1921, **6**, 139; J. Soc. Dyers Col. 1921, **37**, 253; Photo Absts. 1921, **4**, 130; Rev. Prod. Chim. 1922, **25**, 23; Chem. Zentr. 1921, IV, 1140. U. S. P. 1502379; abst. C. A. 1925, **19**, 176; J. S. C. I. 1924, **43**, 743. F. P. 536188; abst. Chem. Zentr. 1922, IV, 1195-R; J. Soc. Dyers, 1922, **28**, 291.

6. E. P. 173021; abst. Chim. et Ind. 1922, **8**, 1298.

at above their melting point ( $175^{\circ}$ ), triacetin being added to lower the fusing point<sup>1</sup>.

In the manufacture of cellulose ether filaments<sup>2</sup> where solvents of low boiling point are used, the spinning may be effected at lower temperatures, especially in the presence of formaldehyde or acetaldehyde, and by incorporating in the spinning solutions a solvent or solvents of high boiling point<sup>3</sup>, and submitting the filaments to traction, it is possible to readily draw out the filaments to very fine deniers in dry spinning in a heated atmosphere. If the usual 16% of cellulose ether concentration in the solvents used in filament formation be increased to 20%, filaments of greater strength, rounder cross-section, and showing no tendency to crinkle may be obtained<sup>4</sup>. In the treatment of cellulose ether filaments produced by the dry or evaporative method<sup>5</sup>, an adhesive sizing or dressing is applied to the threads as a combined operation with their production and winding, with or without twisting, the adhesive agent being applied to the traveling threads or yarns of associated filaments. Or<sup>6</sup>, the sizing may be combined as one operation with the production of filaments by applying the sizing to the threads in their travel to the devices on which they are wound as produced<sup>7</sup>. In the obtainment of permanent crepe effects in the manufacture of woven

1. E. P. 174660; abst. C. A. 1922, **16**, 1865; J. S. C. I. 1922, **41**, 248-A; Chim. et Ind. 1923, **10**, 541; Caout. et Gutta. 1922, **19**, 11496; Chem. Zentr. 1922, II, 1065; Kunst. 1923, **13**, 9. Can. P. 248771. F. P. 537650.

2. E. P. 209125; abst. C. A. 1924, **18**, 1576; J. S. C. I. 1924, **43**, 213-B; Chem. Zentr. 1925, I, 1471; Faserstoffe, 1924, **6**, 46. U. S. P. 1669158; abst. J. S. C. I. 1928, **47**, 445-B.

3. E. P. 182166; abst. C. A. 1922, **16**, 4356; J. S. C. I. 1922, **41**, 627-A; Chim. et Ind. 1923, **9**, 1197; Chem. Zentr. 1922, IV, 907.

4. E. P. 210108; abst. C. A. 1924, **18**, 1757; J. S. C. I. 1924, **43**, 251; Ann. Rep. S. C. I. 1924, **9**, 153; Chem. Zentr. 1924, I, 2760; Faserstoffe, 1924, **6**, 67.

5. Can. P. 253168; abst. Chem. Zentr. 1926, I, 3516.

6. E. P. 210266; abst. C. A. 1924, **18**, 1757; Chem. Zentr. 1924, I, 2760; Faserstoffe, 1924, **6**, 67.

7. Belg. P. 314568.

fabrics consisting of or containing cellulose ethers<sup>1</sup>, one employs relatively highly twisted weft yarns which have been provided with a protective coating or dressing serving to resist permanent elongation of the yarn under the effect of the relatively high twist, while conserving the elasticity.

In dyeing cellulose ethers and esters<sup>2</sup>, in spite of the water-repellent properties of fibers, films and other materials consisting of methyl-, ethyl-, or benzyl-cellulose or other cellulose ethers, and although the hydroxyl groups in the cellulose molecule suffer steric hindrance by reason of the etherifying groups present, such materials may be dyed in the normal manner by means of direct cotton and also acid dyestuffs (in a neutral bath) such as Nigrosine B, Alizarine Astrol B, Azo Yellow 3 G, Rocelline and Orange II, the fastness of the resulting shades being improved when necessary by an after treatment of the dyed material with solutions containing copper or chromium salts<sup>3</sup>; basic dyestuffs (no mordant necessary), such as Magenta, Malachite Green, Methyl Violet, Thioflavine T, and Methylene Blue B<sup>4</sup>; and with ice colors and colors produced by oxidation of amino compounds on the fiber, such as Aniline Black and Paramine Brown, the cellulose ethers have an affinity for the bases and developers used; and<sup>5</sup> for vat dyestuffs of the indigo and anthraquinone series. The affinity of the cellulose ethers for basic and acid dyestuffs is good, and when dyeing is carried out in an acid or alkaline

1. E. P. 226256; abst. J. S. C. I. 1925, **44**, 201-B; Chem. Zentr. 1925, I, 2117. Can. P. 247234. U. S. P. 1538030.

2. E. P. 196952; abst. C. A. 1923, **17**, 3794; J. S. C. I. 1923, **42**, 713-A; J. Text. Inst. 1923, **14**, 204-A; J. Soc. Dyers, 1923, **39**, 291; Chem. Zentr. 1923, IV, 619; Faserstoffe, 1924, **6**, 10. F. P. 558917; Chem. Zentr. 1924, I, 1109.

3. E. P. 196953; abst. C. A. 1923, **17**, 3794; J. S. C. I. 1923, **42**, 713-A; J. Text. Inst. 1923, **14**, A204; J. Soc. Dyers, 1923, **39**, 291; Faserstoffe, 1924, **6**, 10; Chem. Zentr. 1923, IV, 619.

4. E. P. 196954; abst. C. A. 1923, **18**, 3794; J. S. C. I. 1923, **42**, 713-A; J. Soc. Dyers, 1923, **39**, 291; J. Text. Inst. 1923, **14**, A-204; Faserstoffe, 1924, **6**, 10; Chem. Zentr. 1923, IV, 619.

5. E. P. 197281; abst. C. A. 1923, **17**, 3794; J. S. C. I. 1923, **42**, 713-A; Chem. Zentr. 1923, IV, 619; Faserstoffe, 1924, **6**, 10.

bath, no hydrolysis of the cellulose ether occurs under the usual conditions of dyeing<sup>1</sup>.

It is a known fact that ribbon and fabrics made of natural silk and non-silk material cannot be weighted advantageously as the non-silk material absorbs the tin salts or other scrooping materials. By using cellulose ether silk with natural silk, or natural silk and non-silk cellulose ether coated, these disadvantages are obviated<sup>2</sup>.

In a method for protecting against light of short wave lengths, Kopp & Joseph<sup>3</sup> describe a light filter absorbing ultraviolet rays containing triphenylmethane and non-glucoside coumarin derivatives. J. Eder<sup>4</sup> protects the skin against sunburn by solution of naphtholsulfonic acids, naphthylamine sulfonic acids or their salts in a solution of cellulose ether of salve-like consistency. According to A. Eichengruen<sup>5</sup>, in order to produce thin films, a solution of cellulose ether, to which is added a material to diminish the adhesiveness of the film produced, is spread in a very thin layer onto a base consisting of another cellulose derivative which is insoluble in the solvent used for the coating film. After evaporation of solvent, the thin film is removed from the base and rolled in an endless band.

The Farbenfabriken vorm. F. Bayer & Co., prepare artificial filaments from cellulose ethers, using saline solutions as a precipitating bath<sup>6</sup>. Examples are calcium chloride solution of 1.3 sp. gr., or crystallized calcium chloride in the molten state at 70°, or zinc chloride solution of

1. Belg. P. 327477.

2. C. Dreyfus, U. S. P. 1508840; abst. C. A. 1924, **18**, 3727.

3. D. R. P. 253334; abst. C. A. 1913, **7**, 433; J. S. C. I. 1913, **32**, 47; Wag. Jahr. 1912, II, **58**, 568; Chem. Zentr. 1912, II, 1999; Chem. Ztg. Rep. 1912, **36**, 636; Zts. Ang. Chem. 1912, **25**, 2548.

4. U. S. P. 1511874; abst. C. A. 1925, **19**, 153; J. S. C. I. 1924, **43**, 967.

5. E. P. 202306; abst. Kunst. 1925, **15**, 101; E. P. 241590; abst. C. A. 1926, **20**, 3567; J. S. C. I. 1927, **46**, 165. U. S. P. 1688457; abst. C. A. 1929, **23**, 277; J. S. C. I. 1929, **48**, 92-B; Plastics, 1929, **5**, 264; Chem. Zentr. 1929, I, 462-R.

6. D. R. P. 352191; abst. J. S. C. I. 1922, **41**, 807-A; Chem. Zentr. 1922, IV, 599; Chem. Ztg. 1922, **46**, 240; Faser. 1922, **4**, 66; Chim. et Ind. 1923, **10**, 543.

1.85 sp. gr. at 40°<sup>1</sup>. Instead of saline solutions, substances may be used which are capable of taking up the solvent of, but do not act as a solvent or swelling agent for, the cellulose ether. A 75% aqueous solution of urea may be used as the precipitant. In the preparation of photographic films according to this firm<sup>2</sup>, benzylcellulose 10, benzol 90, alcohol 10 and triphenyl phosphate are made into solution, and the cellulose ether lacquer flowed onto a glass plate in the usual manner. Other plastifiers as *p*-toluenesulfamid, methyl *p*-toluenesulfonate, naphthalene, esters of oxalic acid, tetrachlorethane, or tetrachloracetanilid may be used with the benzylcellulose. Another series of cellulose ether plastic-inducing bodies has been described<sup>3</sup>, comprising condensing benzyl chloride, benzal chloride, benzyl alcohol, xylyl chloride, or *p*-xylylene chloride on the one hand, with naphthalene, methylnaphthalene, tar oils, phenanthrene, or anthracene, the products being very stable, gas tight and resistant to water and alkalis.

This firm has also described cellulose ethers of obscure composition<sup>4</sup>, obtained by treating natural or modified cellulose with ethylene oxide, its homologues or analogues, with the exception of epichlorohydrin, in admixture with palmitic acid. According to the conditions employed, the substances obtained from either still possess cellulosic

1. D. R. P. 352192, Addn. to D. R. P. 352191; abst. J. S. C. I. 1922, **41**, 807-A; Chem. Zentr. 1922, IV, 599; Chem. Ztg. 1922, **46**, 240; Chim. et Ind. 1923, **10**, 543.

2. D. R. P. 349868; abst. Chem. Zentr. 1922, II, 960. In this connection see D. R. P. 322586.

3. D. R. P. 336476; abst. Kunst. 1921, **11**, 190; Chem. Zentr. 1921, IV, 148; J. S. C. I. 1921, **40**, 577-A; Ann. Rep. S. C. I. 1921, **6**, 139.

4. D. R. P. 363192; abst. J. S. C. I. 1923, **42**, 348-A; Chem. Zentr. 1923, II, 276; Chem. Tech. Uebers, 1923, **47**, 6; Faser. 1923, **5**, 44. In an addition patent (D. R. P. 368413, abst. J. S. C. I. 1923, **42**, 620-A; Chem. Zentr. 1923, II, 755; Chem. Tech. Uebers, 1923, **47**, 77) carbohydrates as starch, cellulose, tragacanth, dextrin and sugar, are treated with homologues and analogues of ethylene oxide (ethylene sulfide, ethylene imide, propylene oxide, trimethylene oxide, methylphenylethylene oxide, diphenylethylene oxide, glycidic acid and esters, fumacylglycidic acid), giving products generally water-soluble and alcohol-insoluble, suitable for plastic masses.

structure but differ from the cellulose employed in increased weight and reactivity, or swell up or dissolve in water or organic solvents. The reaction may be accelerated by addition of catalysts. The products, presumably glycol ethers of cellulose, may be used for preparing varnishes or impregnating materials; they are also easily acetylated, nitrated, etherified or converted into viscose-like substances, which may be used for making films, artificial silks or plastic materials. In the production of transparent dyeings fast to light, solutions of cellulose ethers<sup>1</sup>, and of substituted anthraquinones, both in benzene, are mixed together, and the solvent removed by evaporation. 1-Amino-2-brom-4-toluidoanthraquinone, 1,4-diamino-2-3-phenoxyanthraquinone, and 1,4-di-*p*-toluidoanthraquinone yield blue, red-violet, and green shades respectively.

In a direct method of enlarging photographs<sup>2</sup>, raw photographic paper is coated with a cellulose ether film, followed by a non-hardening coating of gelatin, the thickness of the latter depending upon the degree of enlargement desired, the whole being finally coated with an ordinary negative emulsion. The developed negative is fixed in a non-hardening bath, the film stripped off the cellulosic layer and placed in slightly acid water. In this the film expands, and when the required degree of enlargement has been arrived at, the gelatin is brought onto a sheet of glass or celluloid and dried. In another method<sup>3</sup>, gelatin is coated with a solution of ethylcellulose 5, triphenyl phosphate 0.5, benzene 94.5 and alcohol 5, and similarly treated.

The Farbwerke vorm. Meister Lucius & Bruening<sup>4</sup> use sulfonic derivatives of tetrahydronaphthalene as sol-

1. D. R. P. 365078; abst. J. S. C. I. 1923, **42**, 264-A; Ann. Rep. S. C. I. 1923, **3**, 174; Chem. Zentr. 1923, II, 338; Chem. Tech. Uebers, 1923, **47**, 47.

2. D. R. P. 356561; abst. Phot. Abst. 1923, **3**, 48; Phot. Ind. 1922, 962; Chem. Zentr. 1922, IV, 731.

3. D. R. P. 362030; abst. J. S. C. I. 1923, **42**, 203-A; Chem. Zentr. 1923, II, 72.

4. D. R. P. 368362; abst. J. S. C. I. 1923, **42**, 494-A; Kunst. 1923, **13**, 70; Chem. Zentr. 1923, II, 769.

vents or swelling agents for cellulose ethers. The best starting material is the mixture of *a*- and *b*-tetrahydronaphthalene-sulfonic chlorides (obtained by chlorosulfonation of tetrahydronaphthalene), from which the amides, alkylamides, hydroxyalkylamides and ethers are prepared. The mixture of *a*- and *b*-tetrahydronaphthalenehydroxyethylsulfonamides, obtained from the sulfonamides and ethylene chlorhydrin, is a viscous oil. The mixture of *a*- and *b*-tetrahydronaphthalene-ethylsulfonamides, from the sulfonamides and diethyl sulfate in alkaline solution, is a colorless viscous oil, b.p. 240°—260° at 10 mm. The mixture of *a*- and *b*-tetrahydronaphthalenesulfonamides is a white powder, m.p. 120°—130°. The mixture of the cresol esters of *a*- and *b*-tetrahydronaphthalenesulfonic acids, obtained from commercial cresol, boils at 240°—260° at 10 mm.

Kalle & Co. claims<sup>1</sup> that pliable films, varnishes and artificial leathers which stand the cold well are obtained by the addition of ethylenethiohydrin or its esters to cellulose derivatives, and that excellent plastics are obtainable when cellulose<sup>2</sup> compounds are treated with the esters of aryloxyacetic acids or their halogen-substituted derivatives and cyclohexanol or its homologues. The cyclohexyl esters of phenoxyacetic acid and 2,4,6-trichlorophenoxyacetic acid prepared from the components by heating in the presence of a little acid, yield celluloid-like or plastic materials with nitrocellulose. These materials are used in the artificial leather industry.

Also<sup>3</sup> that technically useful plastic masses may be formed from substances having both ester and ether characters, such as the alkyl, hydroxyl-alkyl, aralkyl and aryl ethers of *o,o'*-dimethylol-*p*-cresol or esters or aliphatic and

1. D. R. P. 366115; abst. J. S. C. I. 1923, **42**, 348-A; Ann. Rep. S. C. I. 1923, **8**, 151; Kunst. 1923, **13**, 34, 70; Chem. Zentr. 1923, II, 539.

2. D. R. P. 374322; abst. J. S. C. I. 1923, **42**, 1126-A; Chem. Zentr. 1923, IV, 218; Kunst. 1923, **13**, 69.

3. D. R. P. 395704; abst. J. S. C. I. 1925, **44**, 68-B; Ann. Rep. S. C. I. 1925, **10**, 155; Chem. Zentr. 1924, II, 2623; Kunst. 1925, **15**, 122.



aromatic acids and arylsulfonic acids when incorporated with cellulose ethers by the usual methods. Suitable substances are the methoxyl derivatives of *o,o'*-dimethylol-*p*-cresol (m.p. 106°), triacetyl-*o,o'*-dimethylol-*p*-cresol (purified by distillation under reduced pressure, a colorless and odorless oil, b.p. at 12 mm. 212°), and diacetyl-*o,o'*-dimethylol-*p*-cresol *p*-toluenesulphoacid ester (crystallised from alcohol, m.p. 63°), and because of their good gelatinising power are useful for the manufacture of products resembling celluloid and suitable for the artificial leather and film industries.

In dyeing cellulose ethers<sup>1</sup>, slightly basic monoazo dyestuffs containing a sulfamino-group in the diazo-component are particularly suitable for dyeing intense fast shades. Golden-yellow, orange, and reddish-orange dyes are obtained from diazotised 4-aminobenzene-1-sulfamide and aminocresol ether, diazotised 2-nitro-1-aminobenzene-4-sulfamide and *m*-toluidine, and diazotised 4-aminobenzene-1-sulfamide and  $\alpha$ -naphthylamine respectively.

In another process for dyeing cellulose ethers<sup>2</sup>, there is used diethylaniline-*m*-sulfonic acid or substitution thereof, coupled with an unsulfonated aromatic, diazo-compound of the benzene or naphthalene series containing at least one nitro-group. Dyestuffs are obtained which dye cellulose ether filaments deep tints varying from yellow to violet and having good fastness properties.

E. Farrow has added to the list of cellulose ether direct solvents, diluents and plasticizing bodies controlled by the Eastman Kodak Co., supplementing the work of S. Carroll and of J. Donohue, and has called attention to the fact that in the use of cellulose ethers for film formation, it is sometimes desirable to reduce the viscosity of solutions of the same. This may be effectively accomplished, according

1. E. P. 243737; abst. C. A. 1927, **21**, 179; J. S. C. I. 1926, **45**, 628-B; Ann. Rep. S. C. I. 1926, **11**, 153; Chem. Zentr. 1926, I, 2971; Caout. et Gutta. 1926, **23**, 13314.

2. E. P. 243738; abst. Caout. et Gutta. 1926, **23**, 13314; Chem. Zentr. 1926, I, 2971. D. R. P. 450977.

to the patentee, by dissolving the cellulose ether in a mixture of methyl acetate and methyl alcohol, to which about one-seventieth of the weight of the combined solvent, of acetanilid, diphenylamine<sup>2</sup>, benzoic acid<sup>3</sup>, benzamide<sup>4</sup>, tribenzylamine<sup>5</sup>, phenyl benzoate<sup>6</sup>, anthranilic acid<sup>7</sup>, aniline acetate<sup>8</sup>, or benzyl acetone<sup>9</sup> may be added. He has also found that the dyestuff and other coloring matter may readily be removed from waste cellulose ether and other photographic films, by dissolving the latter in any appropriate solvent, and filtration through decolorizing carbon, such as bone char<sup>10</sup>. An apparatus for carrying out the process has been described<sup>11</sup>.

R. Garke, E. Meyer and W. Claasen<sup>12</sup> have described plastic masses obtained by softening benzylcellulose with esters of tetrahydronaphthol as *ar*-tetrahydronaphthol acetate. W. Glover has disclosed a novel method of precipitating cellulose ether filaments, the ether being dissolved in a solvent combination which is a solvent of vegetable oils, this solution being then extruded into the oil (castor, linseed or cod-liver), and the solvent recovered therefrom by

1. U. S. P. 1548938; abst. C. A. 1925, **19**, 3018; J. S. C. I. 1925, **44**, 843; Chem. Zentr. 1926, I, 795; Caout. et Gutta. 1926, **23**, 13315.
2. U. S. P. 1494475; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 2623; Kunst. 1925, **15**, 164.
3. U. S. P. 1494472; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1925, **43**, 593-B; Chem. Zentr. 1924, II, 2716; Kunst. 1925, **15**, 63, 164.
4. U. S. P. 1494471; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 2100; Kunst. 1925, **15**, 164.
5. U. S. P. 1494473; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 2304; Kunst. 1925, **15**, 164.
6. U. S. P. 1494476; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 2716; Kunst. 1925, **15**, 63.
7. U. S. P. 1494470; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 2112; Kunst. 1925, **15**, 164.
8. U. S. P. 1494469; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 1645; Kunst. 1925, **15**, 164.
9. U. S. P. 1494474; abst. C. A. 1924, **18**, 2249; J. S. C. I. 1924, **43**, 593-B; Chem. Zentr. 1924, II, 2439; Kunst. 1925, **15**, 12, 164.
10. U. S. P. 1497137; abst. C. A. 1924, **18**, 2428; J. S. C. I. 1924, **43**, 707; Chem. Zentr. 1924, II, 2112; Kunst. 1925, **15**, 101.
11. E. Farrow and N. Kocher, U. S. P. 1497138; abst. C. A. 1924, **18**, 2428; J. S. C. I. 1924, **43**, 707; Chem. Zentr. 1924, II, 2112; Kunst. 1925, **15**, 101.
12. E. P. 241858; abst. J. S. C. I. 1926, **45**, 152; Ann. Rep. S. C. I. 1926, **11**, 134; Chem. Zentr. 1926, I, 1743. Can. P. 259475.

distillation, the precipitated filaments having been previously removed from the precipitating bath<sup>1</sup>. They have found<sup>2</sup> that cellulose ethers which are insoluble in alkali, when treated with a lower fatty acid with, or without the addition of a suitable catalyst, readily undergo esterification with the formation of cellulose ether-esters. An ethylcellulose approximating in composition to diethylcellulose may be converted by the action of formic, acetic or propionic acids into a diethylcellulose formate, acetate or propionate.

A comprehensive investigation of the benzyl ethers of methylglucoside, glucose, sucrose, lactose, inulin, dextrin, starch and cellulose was published by M. Gomberg and C. Buchler<sup>3</sup> in 1921, benzyl chloride being used as the benzylating agent. Glucose gave an  $\alpha$ -methylglucoside, a tetrabenzyl-benzylglucoside, a benzylglucoside and a dibenzylmethylglucoside; sucrose etherified to monobenzylsucrose, dibenzylsucrose and pentabenzylsucrose; dextrin benzylated to a white, amorphous tasteless powder, melting at about 208-210°. A monobenzylstarch was obtained, melting at 200-203°, and a dibenzylstarch melting at 203-205°. The benzylcellulose obtained was insoluble in Schweitzer's reagent, a tribenzylcellulose, m.pt. 208-210°, a tetrabenzylcellulose, m.pt. 175-177° and a monobenzylcellulose being described with their solubilities. According to N. Grillet<sup>4</sup>

1. U. S. P. 1599230; abst. C. A. 1926, **20**, 3579; J. S. C. I. 1926, **45**, 1010-B; Rev. Gen. Mat. Plast. 1927, #1, 49. E. P. 224405; abst. C. A. 1925, **19**, 1352; J. S. C. I. 1925, **44**, 38-B; Chem. Zentr. 1925, I, 1472; Ann. Rep. S. C. I. 1925, **10**, 154. Can. P. 261967. Ital. P. 235232. Holl. P. 15344.

2. W. Glover and E. van Weyenbergh; U. S. P. 1613451; abst. C. A. 1927, **21**, 649; J. S. C. I. 1927, **46**, 139-B. E. P. 241679; abst. C. A. 1926, **20**, 3567; J. S. C. I. 1926, **45**, 48-B; J. Soc. Dyers, 1926, **42**, 67; Chem. Zentr. 1926, I, 1744; Ann. Rep. S. C. I. 1926, **11**, 130. F. P. 29866, Addn. to F. P. 520101; abst. Chem. Zentr. 1926, I, 1744.

3. J. A. C. S. 1921, **43**, 1904; abst. C. A. 1922, **16**, 59; J. C. S. 1922, **122**, i, 112; J. S. C. I. 1922, **41**, 71-A; Ann. Rep. S. C. I. 1922, **7**, 136; Chem. Zentr. 1922, I, 1396.

4. U. S. P. 1566398; abst. J. S. C. I. 1926, **45**, 152-B; Plastics, 1926, **2**, 134; Chem. Zentr. 1926, I, 2522. E. P. 231837; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1926, **45**, 483. F. P. 592423; abst. Chem. Zentr. 1925, II, 2331. D. R. P. 511793. Swiss P. 124767.

cellulose may be etherified in the presence of a liquid solvent of the desired product, in a large, rotating closed vessel, the Werner-Pfleiderer type<sup>1</sup> being recommended.

In 1924 and 1925 there was published a series of patents by J. Haste for cellulose ether film manufacture. In one<sup>2</sup>, a sensitized layer is carried by a supporting film composed mainly of cellulose ether, cellulose acetate or nitrocellulose, dissolved in butyl or amyl alcohols or acetates, monochloronaphthalene or ethyl propionate or butyrate, and an intervening layer containing a higher percent flexibility-inducing substances than the support layer. In another process there is described the manufacture of a pre-tinted photographic film<sup>3</sup> comprising a photographically sensitive layer, a flexible light-transmitting laminated support which includes two transparent cellulose ether layers interunited through their adjacent faces. The third process<sup>4</sup> involves the production of a photographic film comprising a sensitive layer, a light-transmitting flexible cellulose ether support having a yellowish color, and a layer containing sufficient bluish color to substantially neutralize the yellow color. The fourth process involves a sensitive layer and a support for the same<sup>5</sup>, including two layers of cellulose ester or ether united by a composition containing a hygroscopic substance as glycerol to increase the flexibility. He has described an apparatus<sup>6</sup> for casting cellulose ether films as above described.

The ethers of triphenylcarbinol with cellulose and starch have been investigated by B. Helferich and H. Koes-

1. *Chimie et Ind.* 1920, **1**, 600.

2. U. S. P. 1521881; abst. C. A. 1925, **19**, 616; J. S. C. I. 1925, **44**, 191; Ann. Rep. S. C. I. 1925, **10**, 573.

3. J. Haste and E. Ward, U. S. P. 1486245; abst. C. A. 1924, **18**, 1619; J. S. C. I. 1924, **43**, 451; Chem. Zentr. 1924, II, 791.

4. J. Haste and E. Ward, U. S. P. 1507174; abst. C. A. 1924, **18**, 3557; J. S. C. I. 1925, **44**, 28.

5. J. Haste, U. S. P. 1494479; abst. C. A. 1924, **18**, 2293; J. S. C. I. 1924, **43**, 618; Chem. Zentr. 1924, I, 1087.

6. U. S. P. 1514283. F. P. 558258.

ter<sup>1</sup>. They find that when starch and cellulose (the latter preferably obtained from precipitation of the xanthate) is heated with pyridine and triphenylcarbinol, one of each three hydroxyl groups forms an ether with the triphenylcarbinol. With a large excess of carbinol and prolonged time of reaction, a product of the same composition results, from which the inference is drawn that the two products are chemically more or less homogeneous individuals in which each glucose residue contains an etherified hydroxyl group. This ether union is extraordinarily sensitive to acids. Triphenylmethylcellulose, chlortriphenylmethylcellulose and its corresponding acetate, and triphenylmethylstarch and its acetate have been described in detail. Their technical possibilities have been insufficiently investigated. In another communication triphenylmethyl ethers of isopropyl, propyl, cetyl, allyl alcohol, glycol, glycerol and pyrocatechol are given, together with methods for their formation<sup>2</sup>.

R. Herzog has made a Roentgen-spectrographic investigation of cellulose and its derivatives. In his first communication<sup>3</sup>, the investigation is limited to cellulose, and in the second<sup>4</sup>, includes the cellulose esters and ethers. Cellulose, hydrocellulose and viscose in parallel arrangement show Roentgen diagram similar to that of crystal particles arranged along one axis, whereas nitro-, acetyl- and ethylcellulose are amorphous.

K. Hess<sup>5</sup> in the depolymerisation of cellulose into a biose-anhydride, obtained a *b*-pentacetylglucose by the action of acetyl bromide upon cellulose, and a crystallized bromacetyethyl glucose from treatment of ethylcellulose

1. Ber. 1924, **57B**, 587; abst. C. A. 1924, **18**, 2873; J. C. S. 1924, **126**, i, 500; Chem. Zentr. 1924, I, 2104.

2. B. Helferich, P. Seidel and W. Toeldte, Ber. 1923, **56B**, 766; abst. C. A. 1923, **17**, 2574; J. C. S. 1923, **124**, i, 331; Chem. Zentr. 1923, I, 1166.

3. R. Herzog and W. Jancke, Zts. ang. Chem. 1921, **34**, 385; abst. J. C. S. 1921, **120**, ii, 531. Zts. Physik. 1920, **3**, 196, 343; abst. C. A. 1921, **15**, 983, 1453; Chem. Zentr. 1921, I, 564.

4. R. Herzog, Cellulosechem. 1921, **2**, 101; abst. C. A. 1922, **16**, 1663; J. S. C. I. 1922, **41**, 8-A.

5. Ber. 1921, **54**, 2867; abst. C. A. 1922, **16**, 1400.

with acetyl bromide. Propionyl bromide acts similarly but less energetically.

K. Hess<sup>1</sup>, in checking the work of J. Irvine<sup>2</sup> on the methylation of cotton cellulose obtained the same yield and similar results, but<sup>3</sup> does not agree with E. Heuser in justifying the estimation of the degree of depolymerization of cellulose by determining the molecular weight of the methylated product. They found<sup>4</sup> that acetolysis of ethylcellulose, after action varying in its duration from 2 to 144 hours, gives products which in very dilute solution have molecular weights corresponding with those calculated for a tetraethylbiose anhydride. Depolymerization of cellulose to cellucose occurs therefore, with much greater readiness than has previously been assumed. Molecule weight determinations of tetraethylbiose anhydride were made. They claim that reliable conclusions<sup>5</sup> as to the constitution of cellulose from the products of the acetolysis of alkylated cellulose can be drawn only when the reaction has been carried out in such a way that there is no probability of the disruption of glucoside linkings or of isomerisation. Under these conditions the alkylation stops with the addition of 2 ethyl groups. This appears to be an individual substance and when subjected to the action of acetic anhydride, suffers a marked decomposition, forming the compound  $C_6H_8O_3(OEt)_2$ , in which no CHO group appears to

1. Zts. ang. Chem. 1924, **37**, 993; abst. C. A. 1925, **19**, 1196; J. S. C. I. 1925, **44**, 94-B.

2. J. Irvine and E. Hirst, J. C. S. 1923, **123**, 518; abst. C. A. 1923, **17**, 1956; J. S. C. I. 1923, **42**, 710-A.

3. K. Hess, Zts. Elektrochem. 1925, **31**, 613; abst. C. A. 1926, **20**, 663. K. Hess, W. Weltzein and E. Messmer, Ann. 1923, **435**, 1; abst. C. A. 1924, **18**, 1384; J. S. C. I. 1924, **43**, 88-B; Chem. Zentr. 1924, **1**, 751.

4. K. Hess and W. Wittelsbach, Ber. 1921, **54**, 3232; abst. C. A. 1922, **16**, 2026; J. C. S. 1922, **122**, i, 116; J. S. C. I. 1922, **41**, 94-A; Bull. Soc. Chim. 1922, **32**, 461; Caout. et Gutta. 1922, **19**, 11334; Ann. Rep. S. C. I. 1922, **7**, 136.

5. K. Hess, W. Wittelsbach and E. Messmer, Zts. ang. Chem. 1921, **34**, 449; abst. C. A. 1922, **16**, 490; J. C. S. 1921, **120**, i, 710; J. S. C. I. 1921, **40**, 688-A; Bull. Soc. Chim. 1922, **32**, 56; Chem. Tech. Uebers. 1921, **45**, 327; Paper Trade J. 1922, **74**, 49; Textile Ber. 1922, **43**.

be present. From the mol. wt. (800) it follows that it has at least 4 glucose residues, which must be held together by another system of linkings than that of the glucoside linkings of the original material. The study of various preparations indicates that the depolymerisation is accompanied by isomerization. Further acetylation resulted in the formation of acetylated ethylhexoses. Analyses are given of the reaction products of 75 cc. acetic acid and 75 cc. acetic anhydride upon 52.2 gm. ethylcellulose for 15 hours at 18° (solution) followed by the addition of 25 cc. acetic acid and 25 cc. acetic anhydride with 5.32 gm. 96%  $\text{H}_2\text{SO}_4$  for periods of 1, 3, and 8 hours. The last product, of the approximate formula  $\text{C}_6\text{H}_7\text{O}_2(\text{OEt})_2\text{OAc}$ , sinters 140-50°; on saponification a product is obtained which melts at 95-103°. Upon complete acetylation, a product is obtained with mol. wt. 330, 32.9%  $\text{EtO}$ , 26% acetic anhydride. Upon saponification with  $\text{MeOH-NH}_3$ , triethylglucose is formed, which melts at 99°. Diethylglucose also results.

In their preferred method of cellulose methylation<sup>1</sup>, there is used dimethyl sulfate and hydrated barium hydroxide (which, unlike  $\text{NaOH}$ , does not hydrolyze cellulose or cellulose A) which gives a methylcellulose of 30-40% methoxyl content and which is not effected by alkali, but on methylation with  $\text{NaOH}$  and dimethyl sulfate is converted into trimethylcellulose A of methoxyl content 42-43%. The latter is soluble in cold water, is converted by hydrogen bromide dissolved in glacial acetic acid into acetylbromglucose, the latter on hydrolysis being converted into celluglucosan, which is similar to, but not identical with, ordinary glucosan. From this it is concluded that cellulose consists of glucose anhydride units ( $\text{C}_6\text{H}_{10}\text{O}_5$ ) in a state of association, not in a state of condensation, combination or polymerization.

1. K. Hess, W. Weltzein, E. Messmer, E. Jagla, R. Singer, H. Jensen, A. Reh and F. Kunau, *Ann.* 1923, **435**, 1; *abst. C. A.* 1924, **18**, 1384; *J. S. C. I.* 1924, **43**, 88-B; *Chem. Zentr.* 1924, I, 751.

In a study of trimethylcellulose A and its scission, K. Hess and W. Weltzien<sup>1</sup> used very concentrated alkali (2 of NaOH to 1 of water) in the later stages of the methylation process previously described and, employing a very large excess of alkali over the methyl sulfate, a trimethylcellulose A has been obtained containing approximately 45% OMe. Extensive hydrolysis of the methyl sulfate is avoided by working at lower temperatures (50°-60°). The state of division of the original cellulose is immaterial, but since the solubility of the methylated product in alkali decreases with increasing methoxyl content, improved results are obtained if in the later methylations the material is first dissolved in water and sodium hydroxide added, thereby causing precipitation of the product in a finer state of division. The insolubility of the methylated cellulose appears to protect it against decomposition by the excess of concentrated alkali. The difficulties experienced in obtaining a fully methylated cellulose are attributed partly to the decreasing solubility and partly to a decrease in the acid nature of the cellulose molecule with progressive methylation. The yield of trimethylcellulose A amounts to about 47.5% of the theoretical, after 10 methylations, and identical products are obtained whether barium hydroxide is used in the first four methylations or not. Concordant results in the methoxyl determinations were only obtained by allowing the methylated cellulose to remain for 12 hours at 0° in a sealed tube with hydriodic acid and acetic anhydride before heating for 6 hours at 115°. While cotton cellulose and cellulose A appear to be chemically identical, trimethylcellulose A differs from trimethylcellulose in being soluble in cold water. Trimethylcellulose A, like the insoluble variety, on treatment with 1% methyl-alcohol hydrochloric acid is converted almost quantitatively into trimethylglucose-*α*-methylglucoside, and since trimethylglucose under exactly the same conditions is converted into the *α*-methyl-

1. Ann. 1925, **442**, 46; abst. J. C. S. 1925, **123**, 1, 517; J. S. C. I. 1925, **44**, 238-B.



glucoside, trimethylcellulose A is regarded as possessing the  $\alpha$ -configuration. Hydrolysis of the methylglucoside with 5% hydrochloric acid yields 2,3,6-trimethylglucose; the addition of alkali to an acetone solution of this changes the rotation in two days from  $[\alpha]^{216} = +93.4^\circ$  to  $[\alpha]^{216} = +76.5^\circ$ . Larger excess of alkali produces further changes in the rotatory power. Treatment with acetyl bromide and hydrogen bromide at  $0^\circ$  results in the elimination of at least one methyl group from trimethylcellulose A. Trimethylcellulose A appears to be identical with the product obtained by similar methylation of hydrocellulose; the latter has a slightly lower methoxyl content (44.9% instead of 45.1%), but shows slightly higher rotatory powers in water, acetic acid, and chloroform. Concordant results are obtained on fractionation from cold water, and both products soften and melt at  $230^\circ$ - $237^\circ$ .

In the methylation of cellobiose and the isolation of heptamethyl-methylcellobioside by W. Haworth and E. Hirst<sup>1</sup>, the cellobiose octa-acetate was deacetylated, then methylated in a manner similar to that used by W. Haworth and G. Leitch<sup>2</sup>, hexamethyl-methylcellobioside when isolated, giving 48.2% methoxyl as against 49.3% theory. By thrice digesting this with methyl iodide and silver oxide, crystalline heptamethyl-methylcellobioside was formed; methoxyl found 53.2% against 54.5% for theory.

E. Heuser<sup>3</sup> has made molecular weight determinations of the methyl ethers of various forms of cellulose (containing 2-2.5 methoxyl groups per  $C_6H_{10}O_5$ ) in aqueous solution by the cryoscopic method. The results vary from 6,000 to 8,000 with cotton, to 900 with cellulosedextrin I. Molecular weights decrease with increasing hydration temperature, at which the methyl derivative is precipitated

1. J. C. S. 1921, **119**, 193; abst. C. A. 1921, **15**, 1505; Chem. Zentr. 1921, III, 29.

2. J. C. S. 1919, **115**, 809; abst. C. A. 1919, **13**, 2856; J. S. C. I. 1919, **38**, 691-A; Bull. Soc. Chim. 1920, (4), **28**, 73; Chem. Zentr. 1920, I, 158.

3. Zts. Elektrochem. 1925, **31**, 498; abst. C. A. 1926, **20**, 110; J. C. S. 1925, **128**, 1387.

from aqueous solution on heating, and increase with increasing softening temperature. The results indicate that the alterations in the properties of cellulose brought about by various treatments are due to depolymerization, and conversely that cellulose is a polymerized substance.

It was found by E. Heuser and W. von Neuenstein<sup>1</sup> that methylation of purified cotton gives good yields of dimethylcellulose, only small amounts of water-soluble products being obtained. Hydrocellulose prepared according to E. Knoevenagel and H. Busch<sup>2</sup> is more readily methylated with NaOH and dimethylsulfate than is cellulose itself, and gives good yields of dimethylhydrocellulose, very soluble in cold water, but precipitated when the solution is heated. It is soluble in chloroform, chloroform-alcohol, acetic acid, and pyridine, insoluble in concentrated NaOH. Other methods of methylating hydrocellulose did not give uniform products, although the methoxyl content was sometimes higher. Girard's hydrocellulose<sup>3</sup> yielded a heterogeneous product upon methylation, indicating the original sample was a mixture of unchanged cellulose and hydrolyzed material. Acetylation yielded 30% of a compound, dimethylacetylcellulose (dimethylcellulose acetate), insoluble in water, but dissolving in acetone. The authors<sup>4</sup> conception of dimethylhydrocellulose as a dimethyl derivative of a dimeric anhydrocellobiose is confirmed by cryoscopic determinations of molecular weight in aqueous solution.

E. Heuser and N. Hiemer<sup>5</sup> have made a comprehensive study of the degree of polymerization (i.e. aggregation) of

1. Cellulosechemie, 1922, **3**, 89, 101; abst. C. A. 1923, **17**, 875; J. C. S. 1923, **124**, i, 17; J. S. C. I. 1922, **41**, 977-A; 1923, **42**, 91-A; J. Textile Inst. 1923, **14**, 40-A.

2. Cellulosechemie, 1922, **3**, 42; abst. C. A. 1922, **16**, 2779; Chem. Zentr. 1922, III, 347.

3. A. Girard, Compt. rend. 1875, **81**, 1105; 1879, **88**, 1322; Ann. Chim. Phys. 1881, (5), **24**, 337, 384.

4. E. Heuser and G. Jayne, Ber. 1923, **56**, 1242; abst. C. A. 1923, **17**, 3249; J. C. S. 1923, **124**, i, 657; J. S. C. I. 1923, **42**, 599-A.

5. Cellulosechemie, 1925, **6**, 101, 125, 153; abst. C. A. 1926, **20**, 818; J. S. C. I. 1926, **45**, 502-A; Chem. Zentr. 1926, I, 1391.

alkylated cellulose prepared from physically different celluloses. The following materials were used in the preparation of various methylated celluloses; purified cotton; cellulose regenerated from cuprammonium solutions by carbon dioxide; artificial silk prepared by the cuprammonium process; "hydrocellulose" prepared by the action of hydrochloric acid gas on the same; viscose precipitated by adding a ripened xanthate solution to boiling water; an alkali-soluble "hydrocellulose" formed from viscose silk on treatment with hydrochloric acid gas for 50 hours; "cellulose A," a product formed by Hess and Weltzien's method from the corresponding acetate; "cellodextrin I" prepared by dissolving cellulose in 72-74 per cent sulfuric acid, precipitating (after 1 hour standing) with ethyl alcohol and finally heating with alcohol to insure hydrolysis of cellulose sulfates; "cellodextrin II" prepared by a method similar to that used in the preceding preparation, except that the precipitation with alcohol occurred after the acid solution had remained standing for 10 hours. In general it was found best to limit methylation with a view towards obtaining a product containing 2-2.5 methyl groups for every 6 carbon atoms. The products therefore ranged from 32 to 39 per cent methoxyl and were partially or completely soluble in cold water. Trimethylcellulose preparations are much more insoluble in water and are unsatisfactory for use in molecular weight determinations. Normally, the milder the treatment of the cotton prior to methylation (1) the lower the solubility of the methyl derivative in cold water (2) the higher the molecular weight of the methylated product, (3) the higher its softening point (Erweichungs-temperatur), and (4) the greater the number of methylations required to effect complete methylation of the cellulose. Those methylation products, which are soluble in cold water, are usually reprecipitated on heating the solution and may be partially purified in this way. However, with an increasing "degree of depolymerization," the methylcelluloses become increasingly soluble in warm water. The degree of depoly-

merization of cellulose ("depolymerizationsgrad") is defined as the mean molecular weight of the dimethylated product divided by 190 (190 being the molecular weight of  $[C_6H_8O_8](OMe)_2$ ). There appears to be no correlation between the copper number (Schwalbe) and the degree of depolymerization. The results of Heuser and Hiemer indicate that every depolymerization product of cellulose is characterized by a series of properties which, in most cases, change regularly with the degree of depolymerization. The period of complete methylation of cellulose is greatly shortened by acetylation of the dimethyl derivative of viscose. The monoacetyldimethylcellulose (2.5 gm.), when treated with 50 gm. sodium hydroxide in 50 cc. water and 60 cc. dimethyl sulfate at 60° (in the presence of small quantities of ethyl alcohol) followed by treatment with 45 gm. sodium hydroxide in 45 gm. water and 30 gm. dimethyl sulfate, gave rise to a methylcellulose containing 44.3% methoxyl in a single operation. One further methylation in the presence of solid sodium hydroxide (5 gm.) yielded trimethylcellulose (containing 45.4% methoxyl; theory = 45.6%). Cellulose triacetate prepared from cotton linters in 2-phase methylation yielded a product containing 38.3% methoxyl, on further methylations gave a trimethylcellulose (containing 45% methoxyl), m. 220-5°, fairly soluble in cold water and completely soluble in acetic acid and chloroform.

In a study of the methyl ethers of xylan, E. Heuser and W. Ruppel have prepared methyloxylan and dimethylan, and described their properties<sup>1</sup>, including methods for the preparation of pure xylan<sup>2</sup>. Lignin obtained by the action of hydrochloric acid (sp. gr. 1.2) on sawdust<sup>3</sup>, when treated with dimethyl sulfate and sodium hydroxide, gave

1. Ber. 1922, **55B**, 2084; abst. C. A. 1923, **17**, 390; J. C. S. 1922, **122**, i, 810; Chem. Zentr. 1922, III, 667.

2. E. Heuser, J. prakt. Chem. 1921, **103**, 69; abst. C. A. 1922, **16**, 1082; J. C. S. 1922, **122**, i, 921; Chem. Zentr. 1923, I, 1216.

3. E. Heuser, R. Schmitt and L. Gunkel, Cellulosechemie, 1921, **2**, 81; abst. C. A. 1922, **16**, 490; J. C. S. 1922, **122**, 325; Papierfabrik. 1921, **19**, 81; Chim. et Ind. 1922, **8**, 141.

96% of methyl lignin (20.65% methoxyl content, increasing by repeated methylation to 26.29%), the methoxyl being removable only by repeated treatment with HCl in a sealed tube, when a product is obtained containing 67.45-69.3% carbon and 4.16-4.5% hydrogen. Methyl lignin prepared from this substance contains only 5.79% methoxyl. A sodium hydroxide solution of lignin, prepared at 170° in an autoclave, when etherified with dimethyl sulfate had a methoxyl content of 24.7%.

V. Ipatiev and I. Orlov<sup>1</sup> have described the preparation of cyclohexyl ether, cyclohexylcyclohexene, dicyclohexyl and cyclohexylhexanol of possible technical value as cellulose ether and ester plasticizers. A series of investigations have appeared by J. Irvine and his co-workers on the methylation of photosynthetic sugars producing methylated glucoside<sup>2</sup>; anhydromethylglucoside and its oleate<sup>3</sup>, and mono- and di-methyl anhydromethylglucoside; 2,3,6-trimethylglucose, trimethyl-methylglucoside, heptamethyl-methyl lactoside, diethyldimethyl saccharate and ethyl trimethyl saccharate<sup>4</sup>. From acetylation of cotton cellulose by the method of W. Barnett<sup>5</sup>, and conversion into methylglucoside, a yield of 95.1%-95.5% was obtained. Methylglucosides and methylxylosides from esparto cellulose have also been described<sup>6</sup>. On the other hand<sup>7</sup>, cotton cellulose upon exhaustive methylation yields a product

1. Compt. rend. 1925, **181**, 793; abst. C. A. 1926, **20**, 744; Chem. Zentr. 1926, I, 1641.

2. J. Irvine and G. Francis, I. E. C. 1924, **16**, 1022; abst. C. A. 1924, **18**, 3362.

3. J. Irvine and H. Gilchrist, J. C. S. 1924, **125**, 1; abst. C. A. 1924, **18**, 973; Chem. Zentr. 1924, I, 2102.

4. J. Irvine and E. Hirst, J. C. S. 1922, **121**, 1213; abst. C. A. 1922, **16**, 3071; Chem. Zentr. 1922, III, 1331.

5. J. S. C. I. 1921, **40**, T, 8; abst. C. A. 1921, **15**, 1396; Chem. Zentr. 1921, IV, 146. J. Irvine and E. Hirst, J. C. S. 1922, **121**, 1585; abst. C. A. 1922, **16**, 3468; Chem. Zentr. 1923, I, 1426. See also E. P. 24382, 1910; abst. C. A. 1911, **5**, 3157; J. S. C. I. 1911, **30**, 616.

6. J. Irvine and E. Hirst, J. C. S. 1924, **125**, 15; abst. C. A. 1924, **18**, 974; Chem. Zentr. 1924, I, 2105. See E. P. 343147.

7. J. Irvine and E. Hirst, J. C. S. Trans., 1923, **123**, 518; abst. C. A. 1923, **17**, 1956; J. S. C. I. 1923, **42**, 710-A; Chem. Zentr. 1923, III, 1603.

containing, as a maximum, 43.8% methoxyl (trimethylcellulose requires 45.5%). This product on methanolysis and subsequent hydrolysis of the resulting substituted methyl glucosides, yields about 80% of the theoretical quantity of crystalline 2,3,6-trimethyl glucose, no other sugar derivative, except a small quantity of a dimethyl glucose being produced.

For increasing the softness of cellulose derivatives<sup>1</sup>, the methyl, ethyl, and amyl sulfones of benzene, toluene and xylene, or ethyl phenylsulfoneacetate (ethyl ester of phenylsulfone-acetic acid) may be used, or<sup>2</sup>, ditolyldisulfoxide, or diphenylsulfoxide. Cellulose ethers are specified.

In the process of starch methylation as carried out by P. Karrer<sup>3</sup>, the starch is rendered soluble, a product containing 2 methoxyl groups dissolving in water, alcohol and chloroform. During this etherification process, the starch reaction with iodine decreases from a blue to a pale yellow. Simultaneously with the methylation, the crystalloid is depolymerized, so that in the methylated product a simple molecule results. Yields of cellobiose octa-acetate from methyl-cellobiose and methyl-cellobiose acetate have been determined<sup>4</sup> and details of the methylation of methylcellobiose given, whereby hexa- and hepta-methyl-methylcellobiose are obtained. A tetramethylglucoseanilid has been described<sup>5</sup>. Details of the methylation of potato starch (for-

1. M. Schmidt, D. R. P. 366116; abst. J. S. C. I. 1923, **42**, 348-A; Ann. Rep. S. C. I. 1923, **8**, 151; Chem. Zentr. 1923, II, 540; Kunst. 1923, **13**, 34, 70.

2. M. Schmidt and J. Voss, D. R. P. 399074; abst. J. S. C. I. 1924, **43**, 905-B; Chem. Zentr. 1924, II, 1644; Kunst. 1925, **15**, 123.

3. Helv. Chim. Acta, 1920, **3**, 620; abst. C. A. 1921, **15**, 61; Chem. Zentr. 1920, III, 880. Paper, 1920, **27**, #11, 24, 34. K. Hess, Zts. Elektrochem. 1920, **26**, 232. Translated by C. West and published in Paper, 1920, **27**, #13, 13; 1920, **27**, #14, 22.

4. P. Karrer and F. Widmer, Helv. Chim. Acta, 1921, **4**, 174; abst. C. A. 1921, **15**, 2629; J. S. C. I. 1921, **40**, 342-A; J. C. S. 1921, **120**, i, 310; Chem. Zentr. 1921, I, 936.

5. P. Karrer and E. Widmer, Helv. Chim. Acta, 1921, **4**, 295; abst. C. A. 1922, **16**, 63; Cellulosechemie, 1921, **2**, 102; Chem. Zentr. 1921, III, 944.

mation of methylostarch)<sup>1</sup>, inulin<sup>2</sup>, and lichenin (reserve-cellulose)<sup>3</sup> have been published by Karrer and his associates, and in which the fact is brought out of the close relationship between lichenin<sup>4</sup> and ordinary cotton cellulose as emphasized by the similarity of their methylation products. Exhaustive methylation of lichenin gives a product containing 41.9% methoxyl, whereas fully methylated cellulose contains 42%-43%. By hydrolysis with hydrochloric acid in methyl alcohol, both methylated cellulose and lichenin give dimethyl- and trimethyl-methylglucosides in similar proportions.

The object of N. Kocher<sup>5</sup> in preparing photographic films is to reduce the shrinkage when subjected to the fluid treatment ordinarily employed in photographic manipulation, before the film base is coated with sensitive layer, and before the perforations are made in the film, and this is accomplished with cellulose ether film particularly when the flexible base comprises water-insoluble ethylcellulose, by treatment with water near the freezing point. In 1921, C. Lehman<sup>6</sup>, one of our former associates, outlined the advancement and industrial possibilities of the cellulose ethers. P. Levene and G. Meyer<sup>7</sup> have described trimethyl-6-phosphoric acid methylglucoside from 2,3,5-trimethylmethylglucoside; 3,5,6-trimethyl-1,2-acetone glucose

1. P. Karrer and C. Nageli, *Helv. Chim. Acta*, 1921, **4**, 185; abst. C. A. 1921, **15**, 2629; J. S. C. I. 1921, **40**, 361-A; *Chem. Zentr.* 1921, I, 934.

2. P. Karrer and L. Lang, *Helv. Chim. Acta*, 1921, **4**, 249; abst. C. A. 1921, **15**, 2631; J. C. S. 1921, **120**, i, 312; *Chem. Zentr.* 1921, I, 935. See also J. Irvine and E. Steele, J. C. S. 1920, **117**, T. 1474.

3. P. Karrer and K. Nishida, *Helv. Chim. Acta*, 1924, **7**, 363; abst. C. A. 1924, **18**, 1817; J. S. C. I. 1924, **43**, 373-B; J. C. S. 1924, **126**, i, 501; *Chem. Zentr.* 1924, I, 2679.

4. P. Karrer, M. Staub, A. Weinhagen and B. Joos, *Helv. Chim. Acta*, 1924, **7**, 144; abst. C. A. 1924, **18**, 1275; J. S. C. I. 1924, **43**, 249-B.

5. U. S. P. 1437810; abst. C. A. 1923, **17**, 879; J. S. C. I. 1923, **42**, 91-A; *Chem. Zentr.* 1923, II, 1122.

6. *Chem. Age (N. Y.)* 1921, **29**, 343; abst. C. A. 1921, **15**, 3742; *Caout. et Gutta.* 1922, **19**, 11198; *Chim. et Ind.* 1921, **6**, 817.

7. J. Biol. Chem. 1921, **48**, 233; abst. C. A. 1922, **16**, 60; *Chem. Zentr.* 1921, III, 1319. See also P. Levene and M. Yamagawa, J. Biol. Chem. 1920, **43**, 323; abst. C. A. 1920, **14**, 3645.

by methylation of monoacetoneglucose; 3.5.6-trimethylglucose from the preceding by hydrolysis at 100°; 3.5.6-trimethyl-methylglucoside from trimethylacetoneglucose; and 3.5.6-trimethyl-2-phosphoric acid methyl glucoside from the preceding substance and phosphorus oxychloride.

Heat-resisting masses from cellulose ethers are prepared<sup>1</sup> by kneading ethylcellulose 300 in sufficient benzene, to which talcum 300 and a small amount of dyestuff are incorporated.

An epitome of the following 39 series of patented processes indicates the published activity of L. Lilienfeld in the cellulose ether field during the quinquennial period beginning 1921.

In the production of alkylcellulose, particularly ethylcellulose<sup>2</sup>, which are insoluble in water at 16° and above, but are soluble or swell in water at lower temperatures, an alkyl ether soluble in water at 16° is treated with caustic alkali and an alkylating agent, the alkali content in the reacting mixture amounting to not less than 0.1 and not more than 0.25 of the quantity of water present. It has been found<sup>3</sup> that ethers of cellulose, starch or dextrin, having very high water-resisting qualities are producable where carbohydrates are treated in the presence of at least 15 parts of 30-50% NaOH to one part of carbohydrate in the usual manner.

1. G. Leysieffer, D. R. P. 343183; abst. Kunst. 1922, **12**, 8; Chem. Ztg. 1921, **45**, 737; Chem. Zentr. 1922, II, 101; Chem. Tech. Uebers. 1923, **47**, 172; Chim. et Ind. 1923, **9**, 354. Belg. P. 309157.

2. U. S. P. 1505043; abst. C. A. 1924, **18**, 3272; J. S. C. I. 1924, **43**, 784-B. E. P. 181395; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1923, **42**, 1126-A; Chem. Zentr. 1922, IV, 963. Aust. P. 101021. Can. P. 248229; abst. C. A. 1925, **19**, 3491. Can. P. 248230, 252955. See U. S. P. 1488355, E. P. 181395, 200834. F. P. 552771; abst. Chem. Ztg. 1923, **47**, 474.

3. L. Lilienfeld, U. S. P. 1488355; abst. C. A. 1924, **18**, 1750; J. S. C. I. 1924, **43**, 374; Chem. Zentr. 1924, II, 1645. E. P. 163017; abst. C. A. 1921, **15**, 3207; J. S. C. I. 1922, **41**, 10-A; Chem. Zentr. 1921, IV, 586. F. P. 534778; abst. Caout. et Gutta. 1922, **19**, 11425; Chem. Zentr. 1922, IV, 248. D. R. P. 488030; abst. C. A. 1930, **24**, 2291. Aust. P. 93928 addn. to 78217.



If it is desired to obtain an alkali-soluble cellulose ether<sup>1</sup>, there is used an alkali of not less than 50% strength, or a mixture of solid NaOH with a saturated solution of the same, in such proportion that the total quantity of alkali present in the reaction mixture and calculated as NaOH, amounts to less than the weight of the air-dried cellulose (cellulose conversion product insoluble in alkali). Or<sup>2</sup>, the cellulose may first be treated with caustic alkali in solid form and incompletely etherified, more concentrated alkali then added, and etherification continued to the stage desired. If the parent cellulosic material is alkali-insoluble<sup>3</sup>, impregnation with powdered NaOH is recommended, the mixture then comminuted, and finally heated with the alkylating agent either as a one-step or two-step process.

To produce an ethylcellulose soluble in 5-10% NaOH solution to a viscous liquid<sup>4</sup>, the cellulose hydrate obtained from viscose or from cuprammonium cellulose solution is treated with an equal weight of NaOH and 40-70% diethyl sulfate, the mass being stirred or kneaded. The temperature is allowed to gradually rise to 40-45° at the rate of 2-3° per 15 minutes, the ether then precipitated and washed to neutrality. In order to produce usable cellulose ethers of a high degree of etherification which dissolve in organic solvents without leaving undissolved fibers<sup>5</sup>, it is preferable to use an alkalic cellulose of low water content as a matter of economy, as a thorough alkylation may be

1. E. P. 203346; abst. C. A. 1924, **18**, 587; J. S. C. I. 1924, **43**, 11-B; Ann. Rep. S. C. I. 1924, **9**, 153; Chem. Zentr. 1924, I, 383.

2. E. P. 163018; abst. C. A. 1921, **15**, 3207; Chem. Met. Eng. 1921, **25**, 340; Chem. Zentr. 1921, IV, 586. Can. P. 222377; abst. C. A. 1922, **16**, 4087; D. R. P. 475884; abst. C. A. 1929, **23**, 3807; Chem. Zentr. 1929, II, 237. Dan. P. 30677. Norw. P. 36952. Cf. L. Lilienfeld, India P. 11141. Ital. P. 199098 199099, 199100. Aust. P. 91246, 97634.

3. U. S. P. 1589606; abst. J. S. C. I. 1926, **45**, 661; E. P. 177810; abst. C. A. 1922, **16**, 3206; J. S. C. I. 1924, **43**, 11; Ann. Rep. S. C. I. 1924, **9**, 153; Chem. Zentr. 1922, IV, 682; Faser. 1924, **6**, 20. F. P. 549525; abst. Chim. et Ind. 1923, **10**, 1130. Can. P. 248231.

4. E. P. 203347; abst. C. A. 1924, **18**, 587; J. S. C. I. 1924, **43**, 11-B; Ann. Rep. S. C. I. 1924, **9**, 153; Chem. Zentr. 1924, I, 525.

5. E. P. 200816; abst. C. A. 1924, **18**, 328; J. S. C. I. 1925, **44**, 67-B; Chem. Zentr. 1923, IV, 808; Faserstoffe, 1924, **6**, 21.

achieved with a minimum consumption of reactants. It is technically possible to produce usable cellulose ethers of a high degree of alkylation in a multi-stage process with corresponding small amounts of alkali and alkylating agent if the cellulosic material used has an alkali content less than 2 molecular proportions of alkali to one molecular proportion of cellulose, and at the same time a water content of less than 0.5 parts by weight to 1 part by weight of air-dry cellulose<sup>1</sup>.

If it is desired to produce an ethylcellulose which is insoluble in water at 16° and above, but swells or dissolves in water below this temperature, an alkali-insoluble cellulosic body is etherified under such conditions that there is present for one part by weight of cellulose, 0.48-2.5 parts by weight of water<sup>2</sup>, and 0.6-3 parts NaOH, the amount of alkali in any case exceeding the weight of water present. In order to prepare water insoluble alkyl and aralkyl cellulose ethers<sup>3</sup>, and which give clear, hard and flexible films, requiring no softeners to increase their flexibility, the cellulose conversion products are treated with 1 part of alkali to 1 part of cellulose, then etherified in the usual manner.

If the initial material is a cellulose ether insoluble in water but soluble in alkali solutions<sup>4</sup>, this may be further

1. E. P. 200834; abst. C. A. 1924, **18**, 469; J. S. C. I. 1925, **44**, 202-B; Chem. Zentr. 1923, IV, 809. U. S. P. 1683831; abst. C. A. 1928, **22**, 4246; J. S. C. I. 1928, **47**, 811-B.

2. E. P. 181393; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1924, **43**, 51; Ann. Rep. S. C. I. 1924, **9**, 153; Caout. et Gutta. 1923, **20**, 11687; Faserstoffe 1924, **6**, 20; Chem. Zentr. 1924, II, 963. Can. P. 220831; abst. C. A. 1922, **16**, 2989; Faserstoffe, 1922, **4**, 143. See U. S. P. 1505043, 1505044.

3. E. P. 200815; abst. C. A. 1924, **18**, 328; J. S. C. I. 1924, **43**, 938; Chem. Zentr. 1923, IV, 808; Faserstoffe, 1924, **6**, 21. Aust. P. 101665.

4. U. S. P. 1589607; abst. C. A. 1926, **20**, 3084; J. S. C. I. 1926, **45**, 661-B. E. P. 177809; abst. C. A. 1922, **16**, 3545; J. S. C. I. 1924, **43**, 11; Chem. Zentr. 1922, IV, 682; Faserstoffe, 1924, **6**, 10; Caout. et Gutta. 1922, **19**, 11497. D.R. P. 488446; abst. C. A. 1930, **24**, 2599. F. P. 549568; abst. Chim. et Ind. 1923, **10**, 1131. Can. P. 248232; abst. C. A. 1925, **19**, 3163; Aust. P. 83400. See also E. P. 177810; abst. C. A. 1922, **16**, 3206.

alkylated or esterified, derivatives such as ethylcellulose formate, acetate or nitrate being formed. In the preparation of cellulose ethers<sup>1</sup>, neither the removal of excess of caustic alkali nor the process of several days ripening (ageing) is necessary, it sufficing to treat cellulose with an alkylating agent directly.

The process of etherification may be conducted directly upon woven textiles, the cloth being mercerized (alkalicellulose formation) then superficially or incompletely etherified in a known manner<sup>2</sup>. It is merely a process for etherification conducted in the presence of a sufficient amount of cellulose ether non-solvent, that the cellulosic product of reaction does not pass into solution in the reacting composition. In order to obviate the tendency to swelling in water of alkylcelluloses<sup>3</sup>, an albumin-precipitating agent as tannin, trichloroacetic acid, phosphotungstic acid, chrome alum, potash alum, aluminum sulfate may be used to treat the ether.

In the preparation of low water content alkalicellulose<sup>4</sup>, especially suitable for etherifying purposes, an alkalicellulose is dried until substantially anhydrous, then treated with dry or only slightly moistened NaOH. In this manner, the quantity of alkali desired may be added with a high degree of accuracy, and its composition and properties correspondingly governed. Etherification of this product is claimed to result in the formation of ethers of

1. U. S. P. 1441989; abst. C. A. 1923, **17**, 1141; J. S. C. I. 1923, **42**, 180-A; Chem. Zentr. 1923, II, 1122. E. P. 163016; abst. C. A. 1921, **15**, 3207; J. S. C. I. 1922, **41**, 10-A; Chem. Zentr. 1921, IV, 586. Can. P. 248228; abst. C. A. 1925, **19**, 3491; Chem. Zentr. 1927, I, 1251.

2. E. P. 234847; abst. J. S. C. I. 1925, **44**, 668-B; Ann. Rep. S. C. I. 1925, **10**, 143; Chem. Zentr. 1925, II, 1824. Aust. P. 107831.

3. U. S. P. 1505044; abst. C. A. 1924, **18**, 3279; J. S. C. I. 1923, **43**, 784-B; Kunst. 1925, **15**, 101. E. P. 181392; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1923, **42**, 1126-A; Chem. Zentr. 1922, IV, 851; Caout. et Gutta. 1923, **20**, 11687. F. P. 552770; abst. Chem. Ztg. 1923, **47**, 474; Chim. et Ind. 1923, **10**, 944. Can. P. 249775. See also E. P. 181393. Aust. P. 94837.

4. E. P. 200827; abst. C. A. 1924, **18**, 469; J. S. C. I. 1925, **44**, 67-B; Chem. Zentr. 1923, IV, 808. U. S. P. 1683681.

high stability and uniformity. Taking advantage of the observation that alkyl and aralkyl ethers of cellulose, starch and dextrin possess a superior adaptability for use as protective colloids<sup>1</sup>, Lillienfeld has described the preparation of emulsions and suspensions, especially colloid solutions of metals as palladium, platinum, iridium, osmium, silver, mercury, copper, tin, sulfur, selenium and tellurium.

By treating solvent naphtha with sulfuric acid<sup>2</sup> an oil is obtained which distils in vacuo between 150 and 300°, and forms an excellent plasticizing agent for ethyl- or benzyl-starch, or ethyl- or benzyl-cellulose, especially useful in the production of celluloids, artificial leather and insulating compositions as for cables, formulae for each being given<sup>3</sup>.

In the dyeing of alkylcelluloses, direct, acid, vat, sulfur or mordant dyestuffs may be used directly if a cellulose ether is employed which is insoluble in water at 16°, but swells or is soluble in water below this temperature<sup>4</sup>. In order to take advantage of the desirable properties of great stability, extreme permanency, ready solubility in an almost unlimited number of solvent and dissolving combinations<sup>5</sup>, they are combined in solution, with dissolved nitro-, acetyl-,

1. U. S. P. 1444257; abst. C. A. 1923, **17**, 1310; J. S. C. I. 1923, **42**, 292-A; Chem. Zentr. 1923, IV, 436. Aust. P. 89859; abst. Chem. Zentr. 1924, I, 2450. Aust. P. 92914 addn. to 89859; abst. Chem. Zentr. 1924, I, 2450.

2. U. S. P. 1625415; abst. C. A. 1927, **21**, 2054; J. S. C. I. 1927, **46**, 518-B; Chem. Zentr. 1927, II, 362. E. P. 163271; abst. C. A. 1922, **16**, 141; J. S. C. I. 1922, **41**, 50-A; Chem. Zentr. 1922, II, 543.

3. U. S. P. 1625416; abst. C. A. 1927, **21**, 2054; J. S. C. I. 1927, **46**, 519-B; Plastics, 1927, **3**, 608. E. P. 171661; abst. C. A. 1922, **16**, 1301; J. S. C. I. 1922, **41**, 53-A; Chem. Zentr. 1922, II, 544; Kunst. 1923, **13**, 9. F. P. 535132; abst. Caout. et Gutta. 1922, **19**, 11495; Chem. Zentr. 1922, IV, 274. D. R. P. 504226; abst. C. A. 1930, **24**, 5444. Can. P. 249773; abst. Chem. Zentr. 1926, I, 2757. Dan. P. 29621. Aust. P. 91680.

4. E. P. 181391; abst. C. A. 1922, **16**, 3763; Ann. Rep. S. C. I. 1923, **8**, 174; Chem. Zentr. 1922, IV, 841; Caout. et Gutta. 1923, **20**, 11687. E. P. 181394; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1923, **42**, 1126-A; Caout. et Gutta. 1923, **20**, 11687; Chem. Zentr. 1922, IV, 771. F. P. 552769; abst. Chem. Zentr. 1924, I, 2742; J. Soc. Dyers. 1923, **39**, 231; Chim. et Ind. 1923, **10**, 944. Aust. P. 97660. Can. P. 249774.

5. U. S. P. 1563205; abst. C. A. 1926, **20**, 465; Plastics, 1926, **2**, 12; Chem. Zentr. 1926, I, 2397.

formyl-cellulose, in conjunction with camphor, naphthalene, rubber, balata, metallic resins and oleates, wax, paraffin, fats and similar bodies, in the insulation art. Water-insoluble ethylcellulose or benzylcellulose with *m*-xylylethane or benzylcresyl ethers dissolved in toluene and ethyl alcohol, is recommended.

In artificial filament production<sup>1</sup>, cellulose alkylation is prolonged but at comparatively low temperatures in order to obtain an ether which is highly dissolvable with low viscosity, so that concentrated solutions may be employed with the minimum of solvent used. Taking advantage of the property of swelling in cold water without actually passing into solution of some of the alkylated celluloses, starches, dextrans, inulins and lichenins<sup>2</sup>, various cosmetics, therapeutic soaps, detergents and disinfectant combinations are possible, by incorporating the medicament with the cellulose ether in the intumesced condition.

It is known that when cellulose hydrate, hydrocellulose or oxycellulose<sup>3</sup> is heated with 30% NaOH solution, it is converted into an alkali-soluble conversion product, so-called acid cellulose<sup>4</sup>. Also this body gives brittle products. If this acid cellulose now be alkylated, as with ethyl chloride or bromide, ethylcelluloses are formed especially applicable to the synthetic filament industry.

When a mono-halogen derivative of a fatty acid is allowed to act upon a cellulose-xanthic acid or a cellulose-

1. F. P. 556781. Can. P. 249776; abst. Chem. Zentr. 1926, I, 2757. Dan. P. 30791. Aust. P. 96997. Norw. P. 37354.

2. Aust. P. 87803; abst. Chem. Zentr. 1922, IV, 904.

3. U. S. P. 1589606; abst. J. S. C. I. 1926, **45**, 661. E. P. 177810; abst. C. A. 1922, **16**, 3206; J. S. C. I. 1924, **43**, 11; Ann. Rep. S. C. I. 1924, **9**, 153; Chem. Zentr. 1922, IV, 682; Faser. 1924, **6**, 20. F. P. 549525; abst. Chim. et Ind. 1923, **10**, 1130. Can. P. 248231.

4. G. Bumcke and R. Wolfenstein; Ber. 1899, **32**, 2492; abst. J. S. C. I. 1899, **18**, 940; Chem. Zentr. 1899, **70**, II, 752; Meyer Jahr. Chem. 1899, **9**, 300; J. C. S. 1899, **76**, i, 852; Jahr. Chem. 1899, **52**, 1290; Bull. Soc. Chim. 1900, **24**, 620.

xanthate, obscure reactions take place<sup>1</sup>, cellulosic bodies soluble in warm or hot water result, and give films upon evaporation which are transparent, but which are scarcely soluble in water at ordinary temperatures. These new products supply a want in the chemistry and technology of colloids, inasmuch as it leads to new emulsoids, whose solutions in water or aqueous solutions of volatile or liquid solvents, yield on drying, clear, shining, pliable layers, which become insoluble in water even during the evaporation or a subsequent heating operation, without becoming opalescent or separating crystals or by-products. They apparently are destined to find application in processes wherein water-soluble colloids as starch, dextrin, glue (gelatin), albumen and gums are now employed, the insolubility in water upon drying being a desirable technical advance. Cellulose xanthic acid (cellulose thionthiolcarbonate) or cellulose xanthate (a salt of the above) is treated with acetic acid to neutrality, then with sodium monochloracetate, when cellulosexanthacetic acid (cellulose thionthiol-carbon-glycolic acid) results, which, when dried directly, comprises scales or skins, or in the anhydrous state, a white powder.

Other derivatives of this series<sup>2</sup> result when not more than 0.5 molecular proportions of the monohalogen fatty acid to one molecular proportion of free NaOH is used. Monochlor-acetic acid, *a*-brom- or *a*-chlor-propionic acid, *b*-iodopropionic acid, bromsuccinic acid or *a*-bromisobutyric acid may be used, and a series of compounds thus obtained. The products may be precipitated from the reaction mixture<sup>3</sup> by the use of an acid, acid salt or an alcohol, and

1. E. P. 231800; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 913-B; Ann. Rep. S. C. I. 1925, **10**, 149; 1926, **11**, 618. D. R. P. 424560; abst. C. A. 1931, **25**, 4401. Belg. P. 325270. Holl. P. 17632. Aust. P. 102305, 116823.

2. E. P. 231810; abst. J. S. C. I. 1925, **44**, 914-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 540.

3. E. P. 231809; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 914-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 275. D. R. P. 516461; abst. C. A. 1931, **25**, 1993. U. S. P. 1682292, 1682294; abst. J. S. C. I. 1928, **47**, 744-B.

are suitable for transparent film formation. In conjunction with an alcohol and a halogenated fatty acid analogous compounds result, especially applicable for films, coatings, adhesives and artificial leather. In conjunction with monochloracetates, ammonia, pyridine, quinoline or guanidine may be used, giving rise to a new series of bodies of technical potentialities<sup>1</sup>. If ammonia and a halogenated fatty acid is allowed to act upon viscose or a cellulosexanthic acid<sup>2</sup>, products result which have high tensile strength in films and filaments. If woven or other textile goods is treated with alkali, then with sodium monochloracetate, the cellulose is superficially or incompletely transformed into products as above, or the fabrics may be treated with a viscose solution, then alkali, and finally a monohydroxy-fatty acid in the form of a water-soluble salt<sup>3</sup>.

If cellulose glycollic acid, cellulose lactic acid or other cellulose hydroxyparaffin-monocarboxylic acid insoluble in cold or hot water but soluble in aqueous alkalis<sup>4</sup> is dissolved in caustic soda, coagulated by sulfuric or acetic acid, ammonium chloride, tannin or formaldehyde, films, filaments and textile finishes of wide applicability are said to result.

When cellulose is acted upon with caustic alkali in the presence of a monohalohydrin of a polyalcohol, a distinct group of new bodies, the oxy- and hydroxy-alkylcelluloses result<sup>5</sup>. *a*-Monochlorhydrin, ethylene chlorhydrin, or epichlorhydrin, acting upon alkalicellulose, produce a series

1. E. P. 231805; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 985-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 796. Aust. P. 122076.

2. E. P. 231802; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 913-B; Ann. Rep. S. C. I. 1925, **10**, 149; 1926, **11**, 618; Chem. Zentr. 1926, I, 274. Aust. P. 102307. U. S. P. 1674405.

3. E. P. 231803; abst. C. A. 1925, **19**, 3600; J. S. C. I. 1925, **44**, 709-B; Chem. Zentr. 1926, I, 782. Aust. P. 105039.

4. E. P. 231811; abst. J. S. C. I. 1926, **35**, 985; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, I, 275. In this connection see E. P. 177810, 203346, 203347.

5. U. S. P. 1722927; abst. J. S. C. I. 1929, **48**, 774-B. E. P. 231807; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 913-B; Ann. Rep. S. C. I. 1925, **10**, 149; 1926, **11**, 618. Aust. P. 108139. Cf. U. S. P. 1502379, 1722928. E. P. 166767, 164374. D. R. P. 363192.

of cellulose chlorhydrins, distinguished by their inertness, stability towards alkali, durability, and transparency and flexibility of the products manufactured from them. If cotton fabric or other woven textile, be impregnated with a chlorhydrin, then submitted to a mercerization step, superficial action ensues, and the luster is materially augmented<sup>1</sup>.

Celluloses thiourethanes may be obtained by causing compounds derived from ammonia in which an alcohol radical is substituted for at least one hydrogen atom of the ammonia, and in which at least one hydrogen atom of the ammonia can be replaced, to react with the products obtained by the action of a monohalogen derivative of a fatty acid on a cellulose xanthic acid or a cellulose xanthate (viscose). These compounds are insoluble or but sparingly soluble in water, soluble in alkalis, and give solutions which upon addition of a precipitant form coagula which may be obtained in transparent films or filaments. These products are sharply differentiated from other cellulose compounds in that they may be worked up into technical products by precipitation of their alkaline solutions, as well as by evaporation of their solutions in volatile solvents. According to whether the alcohol radical is an alkyl, aryl or aralkyl group, these derivatives will be alkylthiourethanes (alkylthio carbamates, alkylxanthamides), or arylthiourethanes (aryl-thiocarbamates, aryl xanthamides), etc. As an example, if sodium cellulose xanthate is treated with sodium chloracetate and aniline there is formed cellulose xanthanilide (cellulose phenylthiourethane). The invention details methods of preparation of cellulose methylthiourethane, cellulose diethylthiourethane, and cellulose phenylethylthiourethane<sup>2</sup>.

1. E. P. 231804; abst. C. A. 1925, **19**, 3600; J. S. C. I. 1925, **44**, 801-B; Ann. Rep. S. C. I. 1925, **10**, 184; Chem. Zentr. 1926, I, 506.
2. E. P. 231801; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 955-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1926, II, 2190. D. R. P. 438918; abst. Chem. Zentr. 1927, I, 1770. Holl. P. 19083. Norw. P. 42811. Swiss P. 118235. Aust. P. 121030, 121031, 121032, 102306. U. S. P. 1674401. Swed. P. 61131.



Analogous bodies<sup>1</sup> such as cellulose ethyl-, phenyl-tolyl- and xylyl-urethane, have been advocated for the manufacture of plastic bodies, in conjunction with thermoplasticizing agents. These cellulose aryl or alkyl urethanes may be etherified in the usual manner with (say) diethyl sulfate<sup>2</sup>, methyl iodide or benzyl chloride, phenyl- or tolyl-thiourethane resulting in the formation of the series methyl-, ethyl-, benzyl-cellulose phenyl (or tolyl) urethane. If cellulose xanthanilide (in the form of alkali salt) is treated with ethyl iodide, ethyl cellulose xanthalide (cellulose phenylimidothiolcarboxylate) results.

Lilienfeld has discovered<sup>3</sup> that strong organic bases, particularly quaternary ammonium bases, or those bases in the aqueous solutions of which a highly electrolytically dissociated hydroxide is assumed to be present, exercise a solvent action upon cellulose, which is enhanced in the presence of alkali. As example of quaternary ammonium bases found suitable, are tetraethylammonium hydroxide, tetramethylammonium hydroxide, or phenyltrimethylammonium hydroxide. These products dissolve cellulose at from room temperature to below zero, and upon spreading upon a surface and precipitating with a dilute acid, transparent products result of technical usefulness.

A series of patents has been granted to W. Lindsay for imparting non-flammability to cellulose ethers and esters. These include addition to the cellulose ether in solution of tricresyl phosphate with calcium sulfate<sup>4</sup>, calcium

1. E. P. 231806; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 985-B; Ann. Rep. S. C. I. 1926, **11**, 618; Chem. Zentr. 1925, II, 2331. Dan. P. 36928. Aust. P. 104709. D. R. P. 467003.

2. E. P. 241149; abst. J. S. C. I. 1926, **45**, 47-B; Chem. Zentr. 1926, I, 2267. Belg. P. 325272, 325273, 329338. Swiss P. 121820, and Addns. 124917, 124918, 124919. Holl. P. 19099. See also E. P. 231802, F. P. 447974, 530891, Holl. P. 29743, India P. 11142, Swed. P. 64340. Aust. P. 108143.

3. E. P. 217166; abst. C. A. 1925, **19**, 398; J. S. C. I. 1924, **43**, 977-B; Chem. Zentr. 1924, II, 2716. Aust. P. 101001.

4. U. S. P. 1493207; abst. C. A. 1924, **18**, 2077; J. S. C. I. 1924, **43**, 553-B; Chem. Zentr. 1925, II, 1757; Kunst. 1925, **15**, 121. E. P. 230663; abst. J. S. C. I. 1925, **44**, 312. Can. P. 260843.

tartrate<sup>1</sup>, calcium sulfate where pyroxylin is present<sup>2</sup>, calcium tartrate where acetylcellulose is present<sup>3</sup>, or where pyroxylin is present. As a nitro-, acetyl- or ethyl-cellulose plastifier<sup>4</sup>, *bb*-dichlorethyl ether has been brought forward. The inflammability of cellulose ethers may be diminished by adding<sup>5</sup> aluminum phosphate, hydrated aluminum fluoride, calcium phosphate, tartrate or citrate, or magnesium dihydrogen-*o*-antimonate<sup>6</sup>.

F. Lovejoy<sup>7</sup> produces motion film strips having the margins of nitrocellulose and the central portion of acetyl- or ethyl-cellulose. The film is flowed over a drum from hoppers having the different dopes to produce strips of alternating composition, the strips of nitrate being slit<sup>8</sup>. L. Malone<sup>9</sup> combines cellulose ethers and esters by means of the common solvent pyridine, while I. Matthews uses<sup>10</sup> *b*-chlorethyl acetate in conjunction with benzene, toluene and xylene.

In one method for the formation of artificial filaments from cellulose ethers or esters<sup>11</sup>, the cellulose compound is dissolved in acetone, filtered, and 40% (based on the cellu-

1. U. S. P. 1493208; abst. C. A. 1924, **18**, 2077; J. S. C. I. 1924, **43**, 553-B; Chem. Zentr. 1924, II, 2100; Kunst. 1925, **15**, 121.

2. U. S. P. 1493209; abst. C. A. 1924, **18**, 2077; J. S. C. I. 1924, **43**, 553-B; Kunst. 1925, **15**, 121; Chem. Zentr. 1924, II, 2623.

3. U. S. P. 1493210; abst. C. A. 1924, **18**, 2077; J. S. C. I. 1924, **43**, 553-B; Chem. Zentr. 1924, II, 2304; Kunst. 1925, **15**, 121.

4. U. S. P. 1620977; abst. C. A. 1927, **21**, 1548; J. S. C. I. 1927, **46**, 388-B; Chem. Zentr. 1927, II, 195.

5. E. P. 233874; abst. C. A. 1926, **20**, 823; J. S. C. I. 1925, **44**, 986; Ann. Rep. S. C. I. 1925, **10**, 573. F. P. 530883; abst. Chem. Zentr. 1925, I, 2050.

6. U. S. P. 1538860; abst. C. A. 1925, **19**, 2131.

7. U. S. P. 1469815; abst. C. A. 1923, **17**, 3919.

8. U. S. P. 1518409; abst. C. A. 1925, **19**, 446; J. S. C. I. 1925, **44**, 152; Ann. Rep. S. C. I. 1925, **10**, 573; Kunst. 1929, **19**, 89.

9. U. S. P. 1429153; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1922, **41**, 807-A; Chem. Zentr. 1922, IV, 1183; Kunst. 1925, **15**, 12.

10. U. S. P. 1469816; abst. C. A. 1923, **17**, 3919; J. S. C. I. 1923, **42**, 1172-A; Chem. Zentr. 1924, I, 267; Kunst. 1924, **14**, 44; Faser. 1924, **6**, 11.

11. Naamlooze Vennootschap Nederlandsche Kunstzijdefabriek and F. Beck, Holl. P. 9656, 20656.

lose ether) of calicum thiocyanate, dissolved in the minimum quantity of water added.

C. Olsen<sup>1</sup> proposes to prepare wrapping tissue of film made from ethyl- or benzyl-cellulose. Benzylcellulose is produced by Pathe Cinema<sup>2</sup>, the products of reaction consisting of benzyl alcohol, benzylcellulose, unaltered benzyl-chloride, sodium chloride and water obtained by the action of benzyl chloride on alkalicellulose, being thoroughly mixed with castor oil (approximately 2.5 liters per 500 gms. cotton) and sufficient methyl alcohol added to dissolve the castor oil and benzyl alcohol. Benzylcellulose separates as an impalpable powder, readily washed free from sodium chloride with water. Castor oil may be replaced by other oils that do not dissolve benzylcellulose and are miscible with benzyl alcohol and the wash alcohol.

For dissolving cellulose ethers<sup>3</sup> fractions of wood oils (wood spirit oils) as described by H. Pringsheim and J. Liebowitz<sup>4</sup>, and comprising methylethyl ketone and higher boiling ketones are advocated. C. Piestrak<sup>5</sup> prepares cellulose ether plastics by the use of benzyl alcohol, ethyl acetate, eugenol or creosote, in conjunction with the lactates or oxalates of methyl, ethyl, propyl, butyl and amyl. H. Plauson obtains cellulose ethers<sup>6</sup> by preparing a highly dispersed cellulose in gel form by means of his colloid mill which has also been used for viscose manufac-

1. U. S. P. 1458592; abst. C. A. 1923, **17**, 2645.
2. F. P. 615349; abst. J. S. C. I. 1927, **46**, 649-B; Chem. Zentr. 1927, I, 1392.
3. E. Pfiffner and M. Ow-Eschingen, E. P. 231161; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1926, **45**, 739-B; Ann. Rep. S. C. I. 1926, **11**, 131; Chem. Zentr. 1925, II, 872. Aust. P. 99665.
4. Ber. 1923, **56**, 2034; abst. C. A. 1923, **17**, 3858; J. C. S. 1923, **124**, i, 1052; Chem. Zentr. 1923, IV, 897. H. Pringsheim and A. Gorgas, Ber. 1924, **57B**, 1561; abst. C. A. 1925, **19**, 240; J. C. S. 1924, **126**, i, 1158; Chem. Zentr. 1924, IV, 2218.
5. F. P. 535466; abst. Chim. et Ind. 1922, **8**, 1080; Chem. Zentr. 1922, IV, 274; Caout. et Gutta. 1922, **19**, 11495.
6. E. P. 183908; abst. C. A. 1923, **17**, 209; J. S. C. I. 1922, **41**, 748-A; Ann. Rep. S. C. I. 1922, **7**, 139; Chem. Zentr. 1922, IV, 1086; Faser. 1923, **5**, 59.

ture<sup>1</sup>, claiming that as unusually uniform non-degraded cellulose ether may be made, when the alkalicellulose particles are subdivided to less than 0.001 mm. in diameter<sup>2</sup>.

J. Reilly<sup>3</sup> has contributed data to show that methylcelluloses yield on distillation, under pressures ranging from 0.5-18 mm., about 50% of a product which is apparently a methylated glucosane, containing approximately the same methoxyl content as the methylcellulose distilled. In addition, water and gases are produced (carbon monoxide and dioxide, and methane).

A. Romahn prepares celluloid-like masses from nitrocellulose or cellulose ethers<sup>4</sup> by the use of acetanilid, J. Stevens having used this anilid for the same purpose in 1893<sup>5</sup>. W. Sachs<sup>6</sup> has proposed to coat paper strips with ethylcellulose in the production of a paper yarn or string. In connection with the methylation of polysaccharides, L. Schmid<sup>7</sup> has tried on cellulose, the action of diazomethane. Although methylation did take place, the results obtained were very unsatisfactory. This is not in accordance with the experience of M. Nierenstein<sup>8</sup>, who, in conjunction with A. Geake<sup>9</sup> obtained from cotton cellulose and

1. E. P. 184533; abst. C. A. 1923, **17**, 210; J. S. C. I. 1922, **41**, 806-A; Ann. Rep. S. C. I. 1922, **7**, 122; Chem. Zentr. 1922, IV, 1182; *Faser*. 1923, **5**, 59.

2. *Zts. ang. Chem.* 1921, **34**, 469, 473; abst. C. A. 1922, **16**, 450.

3. *Helv. Chim. Acta.* 1921, **4**, 616; abst. C. A. 1921, **15**, 3464; *Chim. et Ind.* 1922, **7**, 673; J. C. S. 1921, **120**, i, 545; Chem. Zentr. 1921, III, 946.

4. E. P. 238253; abst. J. S. C. I. 1926, **45**, 580-B.

5. U. S. P. 510617; abst. J. A. C. S. 1894, **16**, 68. 517987; and formilid by J. Schupphaus, U. S. P. 528812. E. P. 21331, 1894; abst. J. S. C. I. 1894, **13**, 1248; *Jahr. Chem.* 1896, **49**, 1031; *Chem. Ztg.* 1896, **20**, 330; *Ber.* 1896, **29**, 452. D. R. P. 80776; abst. *Wag. Jahr.* 1895, **41**, 1088; *Zts. ang. Chem.* 1895, **8**, 397; *Jahr. Chem.* 1895, 1361; *Meyer Jahr.* 1895, **5**, 341.

6. D. R. P. 342097; abst. Chem. Zentr. 1922, II, 48; Chem. Tech. Uebers. 1923, **47**, 132; *Textileberichte*, 1921, **2**, 377.

7. *Ber.* 1925, **58**, 1963; abst. C. A. 1926, **20**, 743; Chem. Zentr. 1926, I, 890.

8. *Ber.* 1925, **58B**, 2615; abst. C. A. 1926, **20**, 1890; J. S. C. I. 1926, **45**, 154-A; Chem. Zentr. 1926, I, 2195.

9. A. Geake and M. Nierenstein, *Zts. physiol. Chem.* 1914, **92**, 149; abst. C. A. 1914, **8**, 3563; J. C. S. 1914, **106**, i, 1146.

diazomethane products with 1.5-4.2% methoxyl, and with L. Schmid and R. Becker<sup>1</sup>, a monomethyl compound with cellulose, starch, inulin, lichenin and mannitol.

A series of individual and mixed solvents has been described by P. Seel, comprising ethylcellulose in conjunction with mesityl oxide<sup>2</sup>, propylene chloride<sup>3</sup>, dichloropropane<sup>4</sup>, propyl, butyl and amyl acetate with methyl alcohol<sup>5</sup>, methyl alcohol and benzene<sup>6</sup>, and ethyl butyrate, benzene and ethyl alcohol<sup>7</sup>. In the treatment of cotton prior to etherification<sup>8</sup>, he soaks the cellulose in 0.25-1.5% sulfuric acid for 2 hours at 170° F., or<sup>9</sup> all the ingredients may be admixed at once and subjected to rapidly repeated impacts in a disintegrating mill with revolving arms. The alkalicellulose may be treated with the etherifying agent<sup>10</sup> in the presence of a large surface of immunized steel to facilitate the reaction. It is also claimed that cellulose ethers of sufficient quality for certain purposes as in the manufacture of electrical insulating coating result<sup>11</sup> by

1. Ber. 1925, **56B**, 1966; abst. C. A. 1926, **20**, 744; Chem. Zentr. 1926, I, 56.
2. U. S. P. 1469826; abst. C. A. 1923, **17**, 3919; J. S. C. I. 1923, **42**, 1172-A; Chem. Zentr. 1924, I, 267; Kunst. 1924, **14**, 44; Faser. 1924, **6**, 11.
3. U. S. P. 1467071; abst. C. A. 1923, **17**, 3788; J. S. C. I. 1923, **42**, 1065-A; Chem. Zentr. 1923, IV, 962; Kunst. 1925, **15**, 27.
4. U. S. P. 1429169; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1922, **41**, 807-A; Chem. Zentr. 1922, IV, 1183; Kunst. 1925, **15**, 12.
5. U. S. P. 1469825; abst. C. A. 1923, **17**, 3919; J. S. C. I. 1923, **42**, 1172-A; Chem. Zentr. 1924, I, 267; Kunst. 1924, **14**, 44; Faser. 1924, **6**, 11.
6. U. S. P. 1405449; abst. C. A. 1922, **16**, 1316; J. S. C. I. 1922, **41**, 248-A; Chem. Zentr. 1922, II, 881; Kunst. 1924, **14**, 156; Caout. et Gutta. 1922, **19**, 11653.
7. U. S. P. 1405448; abst. C. A. 1922, **16**, 1316; J. S. C. I. 1922, **41**, 248-A; Caout. et Gutta. 1922, **19**, 11653; Chem. Zentr. 1922, II, 881; Kunst. 1924, **14**, 156.
8. U. S. P. 1503604; abst. C. A. 1924, **18**, 2963; J. S. C. I. 1924, **43**, 784-B; Chem. Zentr. 1924, II, 2100.
9. U. S. P. 1507210; abst. C. A. 1924, **18**, 3477; Chem. Met. Eng. 1924, **31**, 631; J. S. C. I. 1924, **43**, 904-B; Chem. Zentr. 1924, II, 2716; Kunst. 1925, **15**, 63.
10. U. S. P. 1437820; abst. C. A. 1923, **17**, 879; J. S. C. I. 1923, **42**, 91-A; Chem. Zentr. 1923, I, 1162; Caout. et Gutta. 1923, **20**, 11931.
11. U. S. P. 1464158; abst. C. A. 1923, **17**, 3253; J. S. C. I. 1923, **42**, 765-A; Chem. Zentr. 1923, IV, 808; Kunst. 1924, **14**, 44.

adding all the ingredients separately to the reaction space and then agitating with heat until the desired stage is attained. If a relatively longer time is taken for heating up the material<sup>1</sup>, better and stronger films and sheets may be made from the cellulose ether produced. He claims that cellulose ethers may advantageously be purified by treatment with dilute nitric acid<sup>2</sup>, which has a specific effect markedly superior to that obtained when sulfuric acid is used. The tendency to curl in a cellulose ether film is lessened by applying a cellulose ester solution to the face of the film<sup>3</sup>, and Seel has illustrated an apparatus for so doing. S. Sheppard<sup>4</sup> plasticizes cellulose ethers with hydrogenated carbocyclic compounds such as tetrahydronaphthalene (tetralin) and decahydronaphthalene (dekalin).

An insulating material, more particularly for electrical purposes, has been described as composed of methyl-, ethyl-, propyl-, butyl- or benzyl-cellulose combined with a bitumen<sup>5</sup>, the plastic material being applied directly in a heated condition to the surface which is to be insulated. D. Smith<sup>6</sup> ethylates corn starch and adds to this chlornaphthalene, Japan wax, and benzyl alcohol in the formation of a type impressible stencil sheet. A plastic sheet material has been described<sup>7</sup>, consisting of alternate layers of casein and a cellulose derivative as the ethers, the layers

1. U. S. P. 1437821; abst. J. S. C. I. 1923, **42**, 91-A; Chem. Zentr. 1923, I, 1123; Caout. et Gutta. 1923, **20**, 11931.

2. U. S. P. 1448091; abst. C. A. 1923, **17**, 1887; J. S. C. I. 1923, **42**, 446-A; Chem. Zentr. 1923, IV, 218; Kunst. 1925, **15**, 26; Caout. et Gutta. 1924, **21**, 12092.

3. U. S. P. 1496359; abst. C. A. 1924, **18**, 2428; J. S. C. I. 1924, **43**, 656-B; Kunst. 1929, **19**, 89.

4. U. S. P. 1441181; abst. C. A. 1923, **17**, 1141; J. S. C. I. 1923, **42**, 180-A; Chem. Met. Eng. 1923, **28**, 366; Chem. Zentr. 1923, I, 1122; Kunst. 1923, **13**, 92; 1925, **15**, 26.

5. Siemens-Schuckertwerke G.m.b.H., E. P. 157119; abst. C. A. 1921, **15**, 1954; Chem. Zentr. 1921, II, 784; Kunst. 1923, **13**, 8. This patent is an addition to E. P. 156527; abst. C. A. 1921, **15**, 1772. Swiss P. 97643; abst. Chem. Zentr. 1923, IV, 424; Kunst. 1924, **14**, 90.

6. E. P. 244543; abst. Pulp & Paper, 1927, **25**, 1197. Patent cites E. P. 216648.

7. Soc. Anon. L'Oyonnaxienne, Fabrique de Matieres Plastiques, E. P. 235350; abst. C. A. 1926, **20**, 988; Chem. Zentr. 1926, I, 1077.

being caused to adhere by treatment with a solvent aided by heat and pressure. Ornamental effects are obtained by forming the outer layers of transparent casein and coloring the subadjacent layers of cellulose ether.

The Societe Chimique des Usines du Rhone<sup>1</sup> have patented an apparatus for the manufacture of the cellulose ethers on a large scale, and mechanical details for transformation of the ether into artificial filaments<sup>2</sup>. The Societe pour la Fabrication de la Soie Rhodiaseta<sup>3</sup> prepare films and filaments of cellulose esters and ethers by dissolving the ether together with an albuminous material in water with potassium, sodium, calcium or zinc thiocyanate or isothiocyanate, and coagulating with solution containing sodium sulfate. A mechanical process for filament formation has also been described and illustrated<sup>4</sup>. R. Stinchfield has evolved several cellulose ether solvents and solvent combinations, including tetrachlorethane with methyl, ethyl, propyl and butyl alcohol<sup>5</sup>; methyl, ethyl, propyl or butyl acetate, propionate or butyrate with methyl, ethyl or propyl alcohol<sup>6</sup>; or a mixture of methyl alcohol 70, benzene 30<sup>7</sup>. A. Sulzer of the same firm (Eastman Kodak Co.) has described various methods for antistatic photographic film formation, in which the film support comprises nitrocellu-

1. F. P. 592423; abst. Chem. Zentr. 1925, II, 2331. Ital. P. 236819. Swiss P. 113353. In F. P. 589732; abst. Chem. Zentr. 1925, II, 1827, is described cellulose ether plasticizing bodies of condensation products of ketones with poly-alcohols, specific examples being, acetone-glycerol, propionylacetone-glycerol, cyclohexanone-glycerol and methylethylketone-glycerol.

2. E. P. 236393. Patent cites E. P. 218913; abst. C. A. 1925, **19**, 580.

3. D. R. P. 512160; abst. C. A. 1931, **25**, 1083. Belg. P. 330795.

4. E. P. 233384; abst. J. S. C. I. 1925, **44**, 587; Chem. Zentr. 1927, I, 1089. Swiss P. 108043; abst. Chem. Zentr. 1925, I, 2424.

5. U. S. P. 1432364; abst. C. A. 1923, **17**, 341; J. S. C. I. 1922, **41**, 978-A; Phot. Abst. 1923, **3**, 14; Chem. Zentr. 1923, II, 358; Kunst. 1924, **14**, 91.

6. U. S. P. 1432365; abst. C. A. 1923, **17**, 341; J. S. C. I. 1922, **41**, 978-A; Phot. Abst. 1923, **3**, 14; Chem. Zentr. 1923, II, 358; Kunst. 1924, **14**, 91.

7. U. S. P. 1518417; abst. C. A. 1925, **19**, 576; J. S. C. I. 1925, **44**, 127-B; Chem. Zentr. 1925, I, 1149; Kunst. 1925, **15**, 164.

lose with a cellulose ether<sup>1</sup>, or a cellulose ether layer superposed upon the support<sup>2</sup>, or a layer of cellulose ether and ester as the anti-static backing<sup>3</sup>, or the support comprising a mixed cellulose ester and ether<sup>4</sup>.

In order to obviate tendency to curling of cellulose ether film during formation<sup>5</sup>, the film is first treated with a swelling bath and then with a shrinking bath. An anti-static photographic support<sup>6</sup> may be formed of ethylcellulose 9, ethyl alcohol 60, chloroform 90 and acetone 300, or a composite backing of mixed cellulose acetate and ethylcellulose may be used<sup>7</sup>. Sulzer has described and illustrated a method of coating airplane wings with water-insoluble cellulose ether<sup>8</sup> dissolved in denatured ethyl alcohol and benzene, and an apparatus for casting cellulose ether films<sup>9</sup>.

In the production of cellulose ethers from alkal cellulose and alkyl halides, E. Teupel<sup>10</sup> claims it is advantageous to alkylate in the presence of a small amount of the same salt as that obtained from the alkyl halide and alkal cellulose during the etherification process, a quantity of the salt formed in the reaction being added to the reaction mixture.

1. U. S. P. 1418405; abst. C. A. 1922, **16**, 2645; J. S. C. I. 1922, **41**, 567-A; Phot. Abst. 1923, **3**, 15.

2. U. S. P. 1432366; abst. C. A. 1923, **17**, 498; J. S. C. I. 1922, **41**, 997-A; Phot. Abst. 1923, **3**, 16; Kunst. 1924, **14**, 156.

3. U. S. P. 1432367; abst. J. S. C. I. 1922, **41**, 997-A; Phot. Abst. 1923, **3**, 16; Kunst. 1924, **14**, 156.

4. U. S. P. 1437829; abst. C. A. 1923, **17**, 695; J. S. C. I. 1923, **42**, 119-A; Chem. Zentr. 1923, II, 1163; Kunst. 1924, **14**, 157.

5. U. S. P. 1482717; abst. C. A. 1924, **18**, 946; J. S. C. I. 1924, **43**, 451-B; Kunst. 1925, **15**, 163.

6. U. S. P. 1432368; abst. C. A. 1923, **17**, 498; J. S. C. I. 1922, **41**, 998-A; Kunst. 1924, **14**, 156.

7. U. S. P. 1437828; abst. C. A. 1923, **17**, 695; J. S. C. I. 1923, **42**, 119-A; Chem. Zentr. 1923, II, 1123; Kunst. 1923, **13**, 92; 1924, **14**, 157.

8. U. S. P. 1552808; abst. C. A. 1925, **19**, 3605.

9. A. Sulzer and H. van Derhoef; U. S. P. 1466733; abst. Kunst. 1924, **14**, 180.

10. D. R. P. 408342; abst. J. S. C. I. 1925, **44**, 397-B; Chem. Zentr. 1925, I, 1665. See p. 130, note 5.



Allyl ethers of sugars, dextrin, starches and cellulose<sup>1</sup> are prepared by treating an alkaline solution of the carbohydrate with allyl bromide. The cellulose derivative proved insoluble in all ordinary liquids. A. Trivelli<sup>2</sup> has devised a motion picture film in which the usual pyroxylin base is coated with a varnish of ethylcellulose in butyl (or amyl) alcohol and benzene (toluene or xylene)<sup>3</sup>.

W. Webb has added to the list of cellulose ether solvents by specifying carbon tetrachloride with ethyl alcohol<sup>4</sup>, or with methyl, ethyl, propyl, butyl or amyl acetate<sup>5</sup>; ethylene chlorbromide with methyl or ethyl alcohol<sup>6</sup>; methyl acetate with methyl, ethyl, propyl, butyl or amyl alcohol<sup>7</sup>; ethylene chlorhydrin<sup>8</sup>; benzyl alcohol or phenylethyl alcohol<sup>9</sup>; ethyl benzoate with methyl or ethyl alcohol<sup>10</sup>; or benzyl acetate with these two alcohols<sup>11</sup>. Webb<sup>12</sup> minimizes the curling tendency of a cellulose ether film by applying a sol-

1. C. Tomecko and R. Adams, J. A. C. S. 1923, **45**, 2698; abst. C. A. 1924, **18**, 1650; Chem. Zentr. 1924, I, 1915.
2. U. S. P. 1411677; abst. C. A. 1922, **16**, 1915.
3. U. S. P. 1458256; abst. C. A. 1923, **17**, 2645; J. S. C. I. 1923, **42**, 765-A; Chem. Zentr. 1924, I, 267.
4. U. S. P. 1418413; abst. C. A. 1922, **16**, 2780; J. S. C. I. 1922, **41**, 542-A; Chem. Zentr. 1922, IV, 646.
5. U. S. P. 1434465; abst. C. A. 1923, **17**, 467; J. S. C. I. 1923, **42**, 10-A; Phot. Abst. 1923, **3**, 14; Caout. et Gutta. 1923, **20**, 11931; Chem. Zentr. 1923, I, 643; Kunst. 1924, **14**, 156.
6. U. S. P. 1432373; abst. C. A. 1923, **17**, 341; J. S. C. I. 1922, **41**, 978-A; Phot. Abst. 1923, **3**, 14; Chem. Zentr. 1923, I, 358; Kunst. 1924, **14**, 91.
7. U. S. P. 1432374; abst. C. A. 1923, **17**, 341; J. S. C. I. 1922, **41**, 978-A; Phot. Abst. 1923, **3**, 14; Chem. Zentr. 1923, I, 358; Kunst. 1924, **14**, 91.
8. U. S. P. 1444406; abst. C. A. 1923, **17**, 1329; J. S. C. I. 1923, **42**, 305-A; Chem. Met. Eng. 1923, **28**, 510; Chem. Zentr. 1923, IV, 342; Kunst. 1925, **15**, 26.
9. U. S. P. 1460690; abst. C. A. 1923, **17**, 2957; J. S. C. I. 1923, **42**, 925-A; Ann. Rep. S. C. I. 1923, **8**, 151; Chem. Zentr. 1923, IV, 861; Kunst. 1924, **14**, 44.
10. U. S. P. 1469862; abst. C. A. 1923, **17**, 3919; J. S. C. I. 1923, **42**, 1172-A; Chem. Zentr. 1924, I, 267; Kunst. 1924, **14**, 44; Faserstoffe, 1924, **6**, 11.
11. U. S. P. 1469863; abst. C. A. 1923, **17**, 3919; J. S. C. I. 1923, **42**, 1172-A; Chem. Zentr. 1924, I, 268; Kunst. 1925, **15**, 43; Faserstoffe, 1924, **6**, 11.
12. U. S. P. 1429179; abst. C. A. 1922, **16**, 3758; J. S. C. I. 1922, **41**, 854-A.

vent to the face of a film, stopping the application before the body of the film is attacked.

G. Weissenberger<sup>1</sup> dehydrates and purifies cellulose ethers by absolute ethyl alcohol. In the non-conducting plastic composition or cement known as plastic enamel of L. Wilson<sup>2</sup>, a dissolved cellulose ether is used. G. Young<sup>3</sup> produces carbohydrate ethers by treating cellulose, starch, or dextrin with methyl, ethyl, *n*-propyl, *iso*-propyl or butyl chloride in the presence of a metallic hydroxide at a temperature of 100-150°.

C. Ellis<sup>4</sup> has described products obtained from still gases in the cracking of petroleum, as ethylene, propylene and butylene, which when esterified, as into dipropyl sulfate, ethylpropyl sulfate, may be employed with cellulose and starch for the production of ethylpropyl, dipropyl and similar ethers. A process was disclosed in 1902 in which a cuprammonium cellulose solution was squirted into a precipitating bath consisting of a layer of relatively cold water<sup>5</sup> in which the thread is drawn out, superimposed on a layer of hot water in which the thread is hardened. This method may be modified to permit of the production of threads of 1-3 deniers from solutions of cellulose ethers<sup>6</sup> by reversing the procedure above outlined, so that the thread is drawn out in a hot layer of the liquid, the temperature, depth and nature of which depend on the char-

1. E. P. 226142; abst. C. A. 1925, **19**, 1629; J. S. C. I. 1925, **44**, 706-B; Plastics, 1926, **2**, 134; Ann. Rep. S. C. I. 1925, **10**, 147; Chem. Zentr. 1925, I, 2030; Kunst. 1925, **15**, 223; Schiess. & Spreng. 1925, **20**, 110. F. P. 587486; abst. Plastics, 1926, **2**, 134; Kunst. 1925, **15**, 224.

2. U. S. P. 1389084; abst. C. A. 1922, **16**, 150; Chem. Zentr. 1921, IV, 1261.

3. U. S. P. 1504178; abst. C. A. 1924, **18**, 3272; J. S. C. I. 1924, **43**, 743-B; Chem. Zentr. 1925, I, 2050. E. P. 184825; abst. C. A. 1923, **17**, 878; J. S. C. I. 1922, **41**, 854-A; 1924, **43**, 743-B; Chem. Zentr. 1923, II, 591; Kunst. 1923, **13**, 56; Chim. et Ind. 1923, **10**, 542. F. P. 555279; abst. Chem. Zentr. 1923, IV, 681.

4. U. S. P. 1464153; abst. C. A. 1923, **17**, 3248.

5. E. Thiele, E. P. 8083, 1902; abst. J. S. C. I. 1903, **24**, 550. U. S. P. 710819; abst. J. S. C. I. 1902, **21**, 1393.

6. Farbenfabr. vorm. F. Bayer u. Co., E. P. 194666; abst. J. S. C. I. 1924, **43**, 51-B.

acter of the solution it is desired to spin, afterwards hardening in an underlying cooler liquid arranged to circulate in the direction of travel of the filament. An apparatus has been described for carrying the operation into effect<sup>1</sup>.

Cellulose ether silks suffer the disadvantage of possessing no affinity for substantive of acid dyes, and a small affinity for basic dyes<sup>2</sup>. This disadvantage may be corrected by the use of an alkylcellulose insoluble in water at 16° and above, but swelling or dissolving at temperatures below 16°, especially below 10°, which can be dyed direct with substantive dyes giving full shades. The S. Groves varnish especially adapted to the application of aircraft<sup>3</sup>, comprises dissolved cellulose ethers to which beeswax and paraffin is added to retard evaporation of the varnish while it is being applied.

H. Dreyfus has patented a process<sup>4</sup> and apparatus<sup>5</sup> for cellulose ether silk manufacture involving structural details which are illustrated in the invention. A photomechanical transfer may be made by squeegeeing a support of a cellulose ether upon the photographic layer and stripping them from the former support of<sup>6</sup> the layer. Plastic and elastic masses suitable as celluloid substitutes<sup>7</sup> have been disclosed, consisting of combining benzylcellulose and xylylcellulose in the presence of comparatively small amounts of plastificants. H. Pringsheim<sup>8</sup> in 1922 detailed researches on the methylation and acetylation of starches and inulin, in which were prepared and their properties described,  $\alpha$ -tetra-amylose, octomethyltetra-amylose, tetramethyldiamy-

1. Soc. Générale de la Soie Artificielle Linkmeyer, E. P. 14655, 1907; abst. J. S. C. I. 1908, **27**, 278.

2. L. Lilienfeld, Aust. P. 96996, 1924. See Aust. P. 94837, 96997.

3. S. Groves, U. S. P. 1366256; abst. C. A. 1921, **15**, 951. E. P. 128974.

4. F. P. 561588. See F. P. 678400.

5. F. P. 566385. See E. P. 165519; abst. J. S. C. I. 1921, **40**, 577-A.

6. Rheinisch-Westfälische Sprengstoff, A. G., D. R. P. 380797.

7. Farbenfabr. vorm. F. Bayer u. Co., D. R. P. 384007; abst. Chem. Zentr. 1924, I, 268.

8. Zts. ang. Chem. 1922, **35**, 345; abst. C. A. 1923, **17**, 223.

lose,  $\alpha$ -tetra-amylose acetate, methylsaccharose and tetramethylfructose.

**Progress During the Biennial Period 1926 and 1927.** J. Altwegg and C. Willard<sup>1</sup> purify cellulose ethers based upon the observation that a solution of crude ethers in a suitable solvent becomes gradually colorless upon the addition of a strong acid. By precipitation, a white purified ether is obtained which, when redissolved, gives colorless solutions. Acetic acid is preferred as the solvent, although nitric, hydrochloric, phosphoric and sulfuric acids are claimed as also suitable. In the manufacture of molding powders with a cellulose ether base<sup>2</sup>, as methyl-, ethyl- and benzyl-cellulose, triacetin, *p*-toluenesulfonamide, xylene-alkylsulfonamides, diethyl phthalate, mannol, resorcinol diacetate, nitrobenzene or tricresyl phosphate are used as plastificants, with urea or urea derivatives as stabilizers. In printing on fabrics, threads or fibers of cellulose ethers<sup>3</sup>, a paste of the cellulose ether in lactic acid, acetic acid or acetone is made, and an inert powder as barium carbonate or sulfate or calcium carbonate added as a thickener, together with dextrin, starch or casein. P. Anief<sup>4</sup> has given a resume of our knowledge of the benzylcelluloses.

In the electrodeposition of cellulose ethers from aqueous emulsions, C. Beal and L. Eberlin<sup>5</sup>, have observed that

1. U. S. P. 1599508; abst. C. A. 1926, **20**, 3567; J. S. C. I. 1926, **45**, 1010-B. Soc. Chim. Des Usines du Rhone, F. P. 603791; abst. J. S. C. I. 1926, **45**, 739-B; Caout. et Gutta. 1927, **24**, 13425; Ann. Rep. S. C. I. 1926, **11**, 131.

2. Amer. Cell. & Chem. Mfg. Co., E. P. 249600. Can. P. 269482. F. P. 607465.

3. American Cellulose & Chemical Mfg. Co., Ltd., E. P. 263355; abst. J. S. C. I. 1927, **46**, 185-B; C. A. 1928, **22**, 172. See Tootal Broadhurst Lee Co., Ltd., and R. Foulds, E. P. 263248. British Celanese, Ltd., G. Ellis and E. Greenhalgh, E. P. 244143. E. P. 219349, 224681, 224925, 227183, 237943.

4. Peintures, Pigments, Vernis, 1927, **4**, 376; abst. C. A. 1927, **21**, 3742.

5. U. S. P. 1589324; abst. Plastics, 1926, **2**, 366; J. S. C. I. 1926, **45**, 793-B; Chem. Zentr. 1926, II, 1343. U. S. P. 1476374; abst. J. S. C. I. 1924, **43**, 104-B; Ann. Rep. S. C. I. 1925, **10**, 411; 1926, **11**, 400. E. P. 251979; abst. Kunst. 1929, **19**, 90; Chem. Zentr. 1926, II, 3080. See also E. P. 253085, 253091; U. S. P. 1580795.

the coatings sometimes become impaired from nascent oxygen liberated at the anode when high current is employed. This may be obviated or largely avoided by having in the anode zone during the deposition, a metal which has a greater affinity for nascent oxygen than has the deposited cellulose ether. It is claimed that by the use of phosphorous or phosphoric acids as a medium of reaction, methyl-, ethyl- or benzyl-cellulose, especially the latter, of superior quality for film and filament formation result. Either ortho- or meta-phosphoric acids may be used, and the process is applicable to the production of mixed alkyl ethers, methyl-ethylcellulose being specified<sup>1</sup>.

In the application of coatings and films to rigid objects<sup>2</sup>, a base of acetylcellulose is first deposited and this coated with a solution of cellulose ether in a solvent which is a non-solvent for the cellulose acetate, as benzene, the object being to protect the finish from atmospheric influences. The cellulose ether may be partially or wholly replaced by cellulose propionate or butyrate in benzene. It has been found<sup>3</sup> that in treating fibers, yarns or fabrics of cellulose ethers with tin chloride under certain conditions, and fixing the tin in insoluble form by precipitation, a material increase in weight and volume takes place without substantially impairing the appearance or other desirable qualities of the fiber.

In dyeing cellulose ether goods<sup>4</sup> in tightly knitted, knotted or woven form, such as on cops, bobbins or beams, difficulties usually encountered in obtaining level dyeings are obviated and the penetrative power of the dye increased, by swelling the fibers by the use of an aromatic hydrocar-

1. British Celanese, Ltd., E. P. 269531; Chem. Zentr. 1927, II, 655. F. P. 632616; abst. C. A. 1928, **22**, 3528.

2. British Celanese, Ltd., E. P. 274841; abst. J. S. C. I. 1928, **47**, 782-B; C. A. 1928, **22**, 2273; Chem. Zentr. 1927, II, 2788. F. P. 637113; abst. C. A. 1929, **23**, 704; Plastics, 1929, **5**, 638.

3. British Celanese, Ltd., E. P. 258874; abst. C. A. 1927, **21**, 8135; J. S. C. I. 1928, **47**, 228-B. Compare F. P. 563785; abst. Ann. Rep. S. C. I. 1924, **9**, 166; Kunst. 1924, **14**, 41. Can. P. 273367.

4. British Celanese, Ltd., E. P. 282036; abst. J. S. C. I. 1929, **48**, 169-B; C. A. 1928, **22**, 3787.

bon (benzene, toluene, xylene), unsaturated or saturated hydrocarbon derivative (ethylene dichloride, dichlorethylene, trichlorethylene, perchlorethylene), or alcohol (methyl, ethyl, propyl, butyl, amyl). The air is evacuated from the goods and the dyestuff solution then allowed to enter. The mordant dyeing of cellulose ethers is claimed to be carried out successfully<sup>1</sup> if the ether fibers are previously submitted to a swelling process, chromium acetate, iron chloride or aluminum acetate being used with furfural and acetic acid as the fixative, swelling agents being formic or acetic acid, furfuraldehyde, phenol or pyridine.

In the stripping of dyestuffs or colors from dyed materials comprising or containing cellulose ethers<sup>2</sup>, especially if the articles to be stripped have been dyed by S. R. A. methods, a liquid is used which is both a swelling agent and a solvent for the dye, as benzene, toluene, xylene, trimethylbenzene, ethylbenzene, acetone, tetrachloroethane, dichlorethylene, trichlorethylene, perchlorethylene, methyl or ethyl alcohol, ammonium sulfocyanide or diacetone alcohol. In the production of patterned or effect materials having a basis of methyl-, ethyl- or benzyl-cellulose with suitable plastizing bodies<sup>3</sup>, the pattern material comprises the same material, which is caused to adhere or be imprinted by heat and pressure aided by the plastic present in the goods.

In the manufacture of stockings and like hosiery<sup>4</sup> from warp knitted or circular knitted fabric of or containing cellulose ether filaments, a blank or pattern is stamped or cut out of the fabric by means of a hot cutting tool whereby the threads of cellulose ether become melted or fused together, the longitudinal edges being subsequently sewn.

1. British Celanese, Ltd., G. Rivat and E. Cadgene, E. P. 273693; abst. J. S. C. I. 1928, **47**, 891-B. F. P. 636058.

2. British Celanese, Ltd., E. P. 260289; abst. C. A. 1927, **21**, 3470; J. S. C. I. 1928, **47**, 284-B.

3. British Celanese, Ltd., W. Dickie and J. Rooney, E. P. 248832.

4. British Celanese, Ltd., E. P. 281271.

Where moire effects are to be produced<sup>1</sup>, as ordinarily obtainable by subjecting ribbed fabrics to heat and pressure under certain governable conditions, and the effects are intended to be permanent, where the fabric is composed of cellulose ethers, the effect is said to be lasting, especially where high boilers or plasticizers are employed in conjunction with the ether. In order to increase the volume and weight of the cellulose ether fabric, and to render it more resistant to "slipping" and laddering and to the effect of heat, a treatment with tannin in solution has been recommended<sup>2</sup>.

A process has been delineated<sup>3</sup> in relating to the treatment of fibers by the carbonization treatment, it having been discovered that cellulose ether filaments are unaffected by the usual carbonization as applied to vegetable fibers, as is real silk. To prevent delustering during the treatment, sodium sulfate is added to the carbonizing bath, especially if aluminum chloride is used in the carbonizing process. In weighting cellulose ether textiles or filaments<sup>4</sup>, stannic chloride followed by a soluble silicate or phosphate, is claimed to be superior to treatment with tin chloride alone. To render cellulose ester or ether fabrics immune or less liable to development of faults caused by lack of cohesion or low coefficient of friction existing between the

1. British Celanese, Ltd., E. P. 280195; abst. J. S. C. I. 1929, **48**, 279-B; C. A. 1928, **22**, 3052; Chem. Zentr. 1928, I, 1119. F. P. 643058; abst. C. A. 1929, **23**, 1515.

2. British Celanese, Ltd., E. P. 260290; abst. J. S. C. I. 1928, **47**, 477-B. F. P. 621316; abst. Chem. Zentr. 1927, II, 1316. Compare R. Clavel, E. P. 252661; abst. J. S. C. I. 1927, **46**, 599-B.

3. British Celanese, Ltd., E. P. 274074; abst. J. S. C. I. 1928, **47**, 811-B; C. A. 1928, **22**, 2066. C. Dreyfus, R. Dort and H. Platt, U. S. P. 1725857; abst. J. S. C. I. 1929, **48**, 848-B. Compare Silver Springs Bleaching & Dyeing Co., Ltd., and A. Hall, E. P. 246879; abst. J. S. C. I. 1926, **45**, 317-B. F. P. 636608.

4. British Celanese, Ltd., E. P. 279502; abst. C. A. 1928, **22**, 3052; J. S. C. I. 1929, **48**, 126-B; Rayon, 1928, **6**, #7, 36; 1928, **6**, #4, 13. Cf. E. P. 259899; abst. J. S. C. I. 1927, **46**, 295-B. F. P. 642628. Can. P. 273366.

threads of the fabrics<sup>1</sup>, they are repeatedly impregnated with at least an 8% solution of oleic, stearic, palmitic, sulfo-benzenestearic, sulfonaphthalenestearic, sulfobenzenericin-oleic, sulfophenolricinoleic, and sulfonaphthalenericinoleic acids or their sodium salts.

An ornamental or patterned fabric may be produced by subjecting a woven or knitted fabric of cellulose ether filaments rendered thermoplastic<sup>2</sup>, to a combined wetting and swelling liquid, and then impressing the pattern thereon. Fabrics made of or containing cellulose ethers are treated without loading to increase the friction between the fibers, e.g. to reduce laddering, with one or more organic substances having a solvent action upon the fibers and of at least 5% concentration, such suitable bodies being hydrocarbon (hexane, decane, dodecane, naphthalenes, decanaphthene, undecanaphthene, pinene, sylvestrene, hexahydrobenzene, tetrahydronaphthalene, *a*-chlornaphthalene, *b*-chlornaphthalene); alcoholic and phenolic bodies (glycerol, phenol, cresols, xlenols, hexahydrophenol, *a*-naphthol, resorcinol, catechol, guaiacol, anisol, tetrahydronaphthol, chlorhydrin, chlorphenol); amino compounds or their hydroxy or halogenated derivatives (alkyl or dialkyl aniline, toluidine, xylidine, aniline, benzyaniline, diphenylamine, phenyl- and ethyl-*a*-naphthylamine, chloraniline, chlornaphthylamine, aminophenols, aminonaphthols, alkylaminonaphthols)<sup>3</sup>.

Sizing preparations for yarns and threads of cellulose ether fabrics have been patented<sup>4</sup>, comprising resinsates

1. British Celanese, Ltd., and G. Ellis, E. P. 280989; abst. *Silk Journal*, 1928, **4**, #47, 68; J. S. C. I. 1928, **47**, 85-B; C. A. 1928, **22**, 3537. U. S. P. 1686149; abst. J. S. C. I. 1928, **47**, 854-B. Can. P. 281189; abst. C. A. 1928, **22**, 3051. F. P. 637764; abst. C. A. 1929, **23**, 1290; Chem. Zentr. 1928, II, 2085.

2. British Celanese, Ltd., W. Dickie and H. Halkyard, E. P. 273406; abst. J. S. C. I. 1927, **46**, 747-B.

3. British Celanese, Ltd., and G. Ellis, E. P. 280990; abst. *Silk Journal*, 1928, **4**, #47, 68; J. S. C. I. 1928, **47**, 85-B. Patent cites E. P. 206818; abst. C. A. 1924, **18**, 1207; E. P. 165164; abst. J. Soc. Dyers Col. 1921, **37**, 253; C. A. 1922, **16**, 650; Ann. Rep. S. C. I. 1921, **6**, 140. F. P. 637765; abst. C. A. 1929, **23**, 1290; Chem. Zentr. 1928, II, 2204.

4. British Celanese, Ltd., C. Ryley and G. Awcock, E. P. 244947; abst. J. S. C. I. 1926, **45**, 189-B.



and naphthenates of calcium, magnesium, zinc, aluminum, sodium, potassium or ammonium, dissolved in benzene, toluene, xylene or oil of turpentine. An excellent size is alleged to result from dissolving mastic or dammar, lard and magnesium oleate in xylene<sup>1</sup> in connection with cellulose ether fabrics. If it is desired to impart waterproof or gasproof properties to the ether fabric<sup>2</sup>, or fibers of methyl-, ethyl- or benzyl-cellulose, they are first woven, then, without or with a plasticizer, heat is applied to spread and soften the individual filaments and cement the same more or less into a continuous piece. The fabrics may be fire-proofed<sup>3</sup> by treatment with tricresyl phosphate 50 and hydrated magnesium carbonate 63.6 to each 100 parts of ethylcellulose or other cellulose ether.

Ordinarily in the manufacture of dentures and obturators for cleft palates<sup>4</sup>, precious metals and vulcanite are employed, but A. Burlin, S. Leicester and B. Holman advocate the use of water-insoluble cellulose ethers with plasticizers and ancillary solvents as being less brittle and liable to fracture, and less irritating to the gums. The plasticizers used, of course, must be odorless and water-insoluble. In producing a combined damask effect and dyeing effect by the impregnating, padding or printing of fabrics<sup>5</sup>, cellulose ethers in the dissolved state in combination with phenol and formaldehyde are applied, and then precipitated in such manner as to form the pattern or produce the detail desired.

1. British Celanese, Ltd., C. Ryley and G. Awcock, E. P. 244979; abst. J. S. C. I. 1926, **45**, 189-B.

2. British Celanese, Ltd., T. Woodman and W. Dickie, E. P. 249946; abst. C. A. 1927, **21**, 1019; J. S. C. I. 1926, **45**, 532-B; Ann. Rep. S. C. I. 1926, **11**, 131.

3. C. Burke, U. S. P. 1633067; abst. Plastics, 1927, **3**, 542; J. S. C. I. 1927, **46**, 775-B. DuPont Viscoloid Co., E. P. 289936; abst. C. A. 1929, **23**, 944; J. S. C. I. 1928, **47**, 478-B.

4. E. P. 251373; abst. C. A. 1927, **21**, 1355; Rayon Journal, 1926, **1**, (Sept.) 39.

5. R. Chatham, U. S. P. 1640596; abst. J. S. C. I. 1927, **46**, 872-B; Chem. Zentr. 1927, II, 2573.

H. Chavassieu<sup>1</sup> has proposed to obtain cellulose ether or ester filaments by solution in a volatile water-miscible solvent as acetone, in conjunction with sulfocyanides or iso-sulfocyanides, those of potassium, sodium, ammonium, calcium or zinc, or double salts as ammonium-zinc or calcium-zinc being employed. The sulfocyanide solution may be aqueous or alcoholized. For the ornamentation of fabrics comprising cellulose ethers or esters<sup>2</sup> to obtain metallic or colored effects as in the simulation of old Venetian metallic tapestries of the Renaissance period, R. Clavel produces the same effect distributed on a fabric of cellulose ether by means of a vertical "doctor blade," a paste containing a thickener as acacia, an insoluble powder usually colored, a white mineral or insoluble dyestuff powder, and a swelling agent for the cellulose ether, as acetone.

In the fabrication of cellulose ether filaments by the dry spinning method<sup>3</sup>, the dissolved ether is projected through the usual minute orifices into a warm atmosphere in such manner that the volatile solvent is dissipated, leaving the cellulose ether in filamentous form, and in order that the threads may be of maximum luster and free from glitter, the temperature near the spinning nozzles is maintained at the highest compatible with continuous spinning, and this means just under the boiling point of the solvent used. Or<sup>4</sup>, uniformity of filament may be assured by providing the spinning cells with heating elements of substantially identical construction communicating in parallel

1. U. S. P. 1622368; abst. C. A. 1927, **21**, 1713; J. S. C. I. 1927, **46**, 438-B; Chem. Zentr. 1927, I, 2957. Soc. Pour la Fabrication de la Soie Rhodiaseta, E. P. 246430; abst. C. A. 1927, **21**, 496; Silk Journal, 1927, **4**, #42, 60; Chem. Zentr. 1926, II, 1216. See also F. P. 689800, 677263.

2. R. Clavel, E. P. 269128; abst. J. S. C. I. 1928, **47**, 260-B; C. A. 1928, **22**, 1483; Chem. Zentr. 1927, II, 642.

3. Courtaulds, Ltd., and F. Lewis, E. P. 278814; abst. C. A. 1928, **22**, 2840; J. S. C. I. 1927, **46**, 934; Chem. Zentr. 1928, I, 770. F. P. 633957; abst. C. A. 1928, **22**, 3990. D. R. P. 498418; abst. C. A. 1930, **24**, 3902. Can. P. 282326; abst. C. A. 1928, **22**, 3529. E. P. 273506; abst. Chem. Zentr. 1927, II, 2025.

4. Courtaulds, Ltd., F. Wood and E. Turney, E. P. 281058; abst. J. S. C. I. 1928, **47**, 154-B; Chem. Zentr. 1928, I, 1244.

with supply and discharge mains of such capacity that the flow of water is sufficiently plentiful to limit the temperature drop through the heating elements by about 0.1-0.2°.

In wet spinning of cellulose ether, the filament may be introduced into a setting bath of a saponifiable oil as the precipitating medium<sup>1</sup>. A. Davis has described a stencil sheet<sup>2</sup> of carbohydrate ethers (ethers of starch, inosite and quercite) prepared by ethylating (say) corn starch with diethyl sulfate, and coating the stencil sheet base with ethylstarch dissolved in ethyl acetate to which is added chlornaphthalene, Japan wax and benzyl alcohol.

In order to obviate difficulties due to the use of cellulose ethers which swell greatly in the aqueous impregnated condition, J. Defauchamberge<sup>3</sup> proposes to soak the sheets in a deliquescent inorganic chemical dissolved in water as magnesium chloride and transport in this swollen condition to the place where they are to be used, thus obviating contraction upon loss of moisture. E. Dörr<sup>4</sup> isolates benzyl-cellulose from the crude product obtainable from cellulose benzylation by the use of an inert water-soluble salt as sodium chloride mixed with the crude material, the resulting mixture being then alcohol extracted and the residual salt removed by elutriation with water.

C. Dreyfus manufactures pressed and molded articles from cellulose ether compositions<sup>5</sup> as phonograph records, by combining the ether or ester with *p*-toluene sulfonamide,

1. Courtaulds, Ltd., Can. P. 261967; abst. C. A. 1926, **20**, 3578. Same as E. P. 224405; abst. C. A. 1925, **19**, 1352; J. S. C. I. 1925, **44**, 38-B; Chem. Zentr. 1925, I, 1472. U. S. P. 1599230; abst. C. A. 1926, **20**, 3579; J. S. C. I. 1926, **45**, 1010-B.

2. U. S. P. 1594769; abst. Chem. Zentr. 1926, II, 1707.

3. U. S. P. 1576631; abst. J. S. C. I. 1926, **45**, 356-B; Rayon Journal, 1926, **1**, #3, 46; Rayon, 1926, **2**, #6, 15; Chem. Zentr. 1926, II, 136.

4. U. S. P. 1771529; abst. C. A. 1930, **24**, 4631; J. S. C. I. 1930, **49**, 901-B; Plastics, 1930, **6**, #10, 608. E. P. 265491; abst. J. S. C. I. 1927, **46**, 296-B; C. A. 1928, **22**, 317; Chem. Zentr. 1927, I, 3162. D. R. P. 522170; abst. C. A. 1931, **25**, 3167. Compare U. S. P. 1751685; abst. C. A. 1930, **24**, 2599.

5. U. S. P. 1595506; abst. C. A. 1926, **20**, 3349; Chem. Zentr. 1927, I, 207. See F. P. 631344. Swiss P. 127755. India P. 13467.

xylenemonomethyl sulfonamide, acetin or other suitable plasticizing agent, allowing the mass to solidify, then working up on heated rolls, pigments and resins being incorporated therein if desired. He produces waterproof or gas-proof fabrics or sheet materials by uniting woven or knitted fabrics composed of methyl-, ethyl- or benzyl-cellulose, with other fabrics composed of natural filaments, then compacting by means of heat and pressure<sup>1</sup>. Pattern effects may be impressed on fabrics primarily composed of cellulose ethers<sup>2</sup> in a manner analogous to that above indicated. By combining cellulose ether fabrics with other fabrics by means of a thermoplastic, heat and pressure. C. Dreyfus and G. Miles<sup>3</sup> mix with a cellulose ether or ester a proportion of a hygroscopic substance as zinc chloride in order that the film may retain a given amount of moisture under normal atmospheric conditions, and still retain its flexibility.

In dyeing and printing fabrics composed of or containing cellulose ethers and esters, H. Dreyfus<sup>4</sup> first loads the fabrics with tin, zinc, tungsten or aluminum phosphate or silicate or with a tannin solution to increase their affinity for dyestuffs. It has been found<sup>5</sup> that augmented quantities of loading agents may be introduced into cellulose ethers and esters if the material is treated with aqueous solutions of swelling agents, as glycollic acid or lactic acid, before or during the loading stage of the fabric. Suitable swelling solutions are aqueous solutions containing either 7-10% acetone, 50% ethyl alcohol, 15-20% diacetone alcohol or 10-12% ammonium thiocyanate. For

1. C. Dreyfus, E. P. 248147; abst. Chem. Zentr. 1926, II, 2855.

2. C. Dreyfus, E. P. 254354; abst. J. S. C. I. 1926, **43**, 785-B; Chem. Zentr. 1927, I, 1374. U. S. P. 1634613. F. P. 609483.

3. U. S. P. 1611169; abst. C. A. 1927, **21**, 496; J. S. C. I. 1927, **46**, 228-B; Chem. Zentr. 1927, I, 2146.

4. E. P. 272982; abst. C. A. 1928, **22**, 1859; J. S. C. I. 1927, **46**, 650; Chem. Zentr. 1927, II, 2573; Die Kunstseide, 1927, **9**, 525. Belg. P. 352472. F. P. 621316.

5. H. Dreyfus, E. P. 281084; abst. C. A. 1928, **22**, 3528; J. S. C. I. 1928, **47**, 227-B; Chem. Zentr. 1928, I, 1732. F. P. 634165. Tin thiocyanate (F. P. 642331) has also been specified.

ornamenting fabrics of cellulose ethers or esters to produce moire effects thereon<sup>1</sup>, transparent or translucent sheets of cellulose ether are used for the close line patterns or grid patterns which are impressed on the sheets. He produces figured bodies of moldable material by taking a textile fabric containing cellulose ether or ester, adding a cellulose ether plastic in powdered condition to form the pattern, then compressing with heat and pressure to produce a unitary appearing layer<sup>2</sup>.

In preparing cellulose ethers wherein cellulose is treated with a halogen compound of glycol or other polyhydric alcohol, H. Dreyfus<sup>3</sup> takes up the water formed in the reaction by a material capable of combining therewith as calcium, magnesium, calcium hydroxide, magnesium hydride, sodamide or sodium ethylate powder. For example, cellulose is mixed with water and sodium hydroxide plus calcium oxide, the mixture being kneaded while cooled. Ethylene oxide or ethylene chlorhydrin is then added at 0°, forming a cellulose ether.

In the dyeing of cellulose ethers and esters<sup>4</sup>, *o*-amino-thraquinone sulfonic acids have been found to exert a strong affinity, giving yellow, orange, red and violet dyeings depending upon the particular anthraquinone sulfonic acid derivative used. Whereas most of the known azo dyes have no affinity for the cellulose ethers<sup>5</sup>, it has been found that when such products as ammonium 2,6-dinitroaniline-4-sulfonate, ammonium 2,6-dinitroaniline-6-sulfonate or am-

1. H. Dreyfus, Can. P. 262843; abst. Chem. Zentr. 1927, II, 1904. Same as E. P. 250658; abst. Chem. Zentr. 1926, II, 2367.

2. H. Dreyfus, F. P. 606536; abst. Chem. Zentr. 1927, I, 3139; Kunst. 1926, 16, 206. Can. P. 270404.

3. H. Dreyfus, E. P. 277721; abst. C. A. 1928, 22, 2663; J. S. C. I. 1927, 46, 872-B; Plastics, 1928, 4, 509; Chem. Zentr. 1928, I, 445.

4. W. Duisberg, W. Hentrich, C. Weinand and L. Zeh, U. S. P. 1587708; abst. C. A. 1926, 20, 2588; J. S. C. I. 1926, 45, 741-B; Ann. Rep. S. C. I. 1926, 11, 116; Plastics, 1927, 3, 82; Chem. Zentr. 1927, I, 522. D. R. P. 433236; abst. Chem. Zentr. 1926, II, 2231.

5. W. Duisberg, W. Hentrich and L. Zeh, U. S. P. 1595178; abst. C. A. 1926, 20, 3352; J. S. C. I. 1926, 45, 781-B; Chem. Zentr. 1927, I, 364.

monium 2,6-triaminobenzene-4-sulfonate are diazotized in the usual manner and coupled with aniline or similar compounds, reddish, violet and brown shades are obtained of great fastness. It has also been found that shades ranging over practically the entire color scale of great penetrative power for cellulose ethers and esters are possible, when ethylcellulose, for example, is dyed directly in an aqueous bath containing the sodium salts of 1,4-diaminoanthraquinone-N-methyl sulfonic acid, 1,5-dihydroxy-4,8-diaminoanthraquinone-N-methyl sulfonic acid, 1,4,5,8-tetraaminoanthraquinone-N-methyl sulfonic acid or *b*-aminoanthraquinone-N-methyl sulfonic acid compounds<sup>1</sup>.

E. Du Pont de Nemours Co.<sup>2</sup> employ in cellulose ether and ester lacquers, tetrahydrofurfuryl alcohol as a high boiler in conjunction with other solvents. In the electrodeposition of coatings of cellulose compounds as water-insoluble ethylcellulose<sup>3</sup>, it has been found that the deposited cellulose ether particles will form into a coating having the desired properties if a suitable solvent or coalescing agent is present in the droplets, or in the liquid containing the droplets. L. Eberlin and C. Beal<sup>4</sup> have also found that aqueous emulsions containing a water-insoluble ethylcellulose in the disperse phase, and one or more coalescing agents, are especially useful in coating electroconducting surfaces by electrodeposition, the coalescing agent entering the coating with the cellulosic compound, causing particles of the latter to blend into a firm skin. P. Ehrman<sup>5</sup> has

1. W. Duisberg, W. Hentrich and L. Zeh, U. S. P. 1609702; abst. C. A. 1927, **21**, 330; J. S. C. I. 1927, **46**, 139-B; Chem. Zentr. 1927, I, 1215.

2. E. P. 279520; abst. C. A. 1928, **22**, 3056; J. S. C. I. 1929, **48**, 293-B; Chem. Zentr. 1928, I, 990.

3. L. Eberlin and C. Beal, U. S. P. 1589327; abst. J. S. C. I. 1926, **45**, 793-B; Chem. Zentr. 1926, II, 1344.

4. L. Eberlin and C. Beal, U. S. P. 1589328; abst. J. S. C. I. 1926, **45**, 793-B; Chem. Zentr. 1926, II, 1344.

5. Thesis Strasbourg; Caout. et Gutta. 1926, **23**, 13030; abst. C. A. 1926, **20**, 3805; Pulp, Paper Mag. 1927, **25**, #23, 740. Compare H. Dreyfus, D. R. P. 322586; Farbenfabriken vorm. F. Bayer & Co., E. P. 164374; G. Young, E. P. 184825.

given a general resume of our knowledge of the cellulose ethers as a part of an Inaugural Thesis at Strasbourg.

In the dyeing of cellulose ethers, golden yellow to reddish-violet tints are obtainable<sup>1</sup> by diazotizing 3-nitro-2-methyl-1-aminobenzene or 3-nitro-2-methyl-1-aminobenzene with diethylaniline-*m*-sulfonic acid; or 4-chlor-2-nitro-1-aminobenzene-1-carboxylate with diethylaniline-*m*-sulfonic acid, these monoazo dyestuffs giving excellent fastness to light. In the dyeing of yarns of cellulose ethers or esters<sup>2</sup>, relatively water-insoluble dyestuffs are solubilized and rendered more receptive to the fiber by the use of sodium or ammonium salts of sulfo-ricinoleic, sulfo-oleic, sulfo-palmitic and sulfo-stearic acids. Or<sup>3</sup>, sodium salts of naphthenic and naphthene sulfonic acids may be used for the same purpose. In mordanting yarn comprising methyl-, ethyl- or benzyl-cellulose, sodium, potassium, ammonium, iron, aluminum or chromium thiocyanate may be used<sup>4</sup>, the amount required being governed by the depth of shade desired. In dyeing red to orange tones on cellulose ether filaments, the dyestuffs from 5-nitro-2-anisidin and benzyl-*o*-sulfanilic acid, or 2,4-dinitroanilin and 4-sulfobenzyl-2-toluidin, or 6-chlor-2-toluidin and 4-sulfobenzyl-2-toluidin, or 2,4-dinitroanilin and N-benzylanthranilic acid may be used<sup>5</sup>.

In the production of uniformly loaded conductors used for signalling purposes<sup>6</sup>, there is tightly wound round the

1. H. Eichwede and E. Fischer, U. S. P. 1599748; abst. C. A. 1926, **20**, 3578; J. S. C. I. 1926, **45**, 1011-B; Ann. Rep. S. C. I. 1926, **11**, 115; Chem. Zentr. 1927, I, 522.

2. G. Ellis, U. S. P. 1618413; abst. J. S. C. I. 1927, **46**, 249-B; Chem. Zentr. 1927, II, 1904.

3. G. Ellis, U. S. P. 1618414; abst. J. S. C. I. 1927, **46**, 249-B; Chem. Zentr. 1927, II, 1904.

4. G. Ellis, U. S. P. 1757519; abst. J. S. C. I. 1930, **49**, 555-B. E. P. 280698; abst. C. A. 1928, **22**, 3305; J. S. C. I. 1928, **47**, 86-B; Silk Journal, 1928, **4**, #47, 68; Chem. Zentr. 1928, I, 1096. F. P. 644565; abst. C. A. 1929, **23**, 1759.

5. Farbenfabriken vorm. F. Bayer & Co., D. R. P. 423601; abst. J. S. C. I. 1926, **45**, 536-B; Chem. Zentr. 1926, I, 2846. D. R. P. 418940, Addn. to D. R. P. 423601; abst. Chem. Zentr. 1926, I, 1044. E. P. 225862; abst. C. A. 1925, **19**, 1632; J. S. C. I. 1925, **44**, 583-B; Ann. Rep. S. C. I. 1925, **10**, 135; Chem. Zentr. 1925, I, 2662.

6. Felten & Guillaume Carlswerk A. G., Can. P. 257645.

conductor a strip made of cellulose ether, the conductor then being surrounded with loading material and placed in acetone to dissolve the strip, finally annealing it. E. Fischer<sup>1</sup> dyes cellulose ethers and esters by disazo dyestuffs containing not more than one naphthalene nucleus, at most one sulfo group, and at least one amino group, prepared by coupling one mole of a mono- or di-hydroxy derivative of benzene or naphthalene series with two molecular proportions of a diazo compound. Or<sup>2</sup>, for the production of yellow shades, *p*-phenylenediamine, or acetyl-*p*-phenylenediamine, or metachloraniline is coupled with *p*-cresol.

W. Glover and C. Topham<sup>3</sup> produce cellulose ether artificial silk by a dry-spinning process involving projecting the filaments into warm air whereby the solvent is vaporized, then leading the filaments in association from the warm space and collecting them in a rapidly rotating spinning box. In producing mixed cellulose ether-esters<sup>4</sup>, a water-insoluble ethylcellulose is treating with an acetylating agent containing acetic anhydride. The ethylcellulose acetate produced contains not more than one ethyl group for each  $C_6H_{10}O_6$ , and not less than 4% ethyl. The product is claimed as especially suitable for film and filament formation, being soluble in acetone and of high viscosity.

1. U. S. P. 1755640; abst. J. S. C. I. 1930, **49**, 554-B; C. A. 1930, **24**, 2897. E. P. 258611; abst. J. S. C. I. 1927, **46**, 874-B; Chem. Zentr. 1927, I, 1215. D. R. P. 477507; abst. C. A. 1929, **23**, 4350; Chem. Zentr. 1929, II, 656.

2. E. Fischer and C. Müller, U. S. P. 1765142; abst. J. S. C. I. 1930, **49**, 945-B; 1931, **50**, 763-B; C. A. 1930, **24**, 4171. E. P. 269934; abst. J. S. C. I. 1928, **47**, 121-B; C. A. 1928, **22**, 1482; Chem. Zentr. 1927, II, 1092. D. R. P. 469514; abst. C. A. 1929, **23**, 1287; Chem. Zentr. 1929, I, 1274. F. P. 632887; abst. C. A. 1928, **22**, 3535.

3. U. S. P. 1665958; abst. J. S. C. I. 1928, **47**, 364-B. E. P. 268455; abst. C. A. 1928, **22**, 1474; J. S. C. I. 1927, **46**, 472-B; Chem. Zentr. 1927, II, 654. D. R. P. 481945; abst. C. A. 1930, **24**, 500.

4. W. Glover and C. Diamond, U. S. P. 1763428; abst. C. A. 1930, **24**, 3900; J. S. C. I. 1930, **49**, 708-B. E. P. 268552; abst. J. S. C. I. 1927, **46**, 473-B; C. A. 1928, **22**, 1473; *Plastics*, 1928, **4**, 508; Chem. Zentr. 1927, II, 655.



In the dyeing of cellulose ethers according to the A. Goeschke method<sup>1</sup>, indophenols as from 2,6-dichlor-4-aminophenol and dimethylaniline give blues of excellent brilliancy and fastness. The N. Grillet method of cellulose ether filament formation owes its alleged claim to inventive ingenuity to mechanical features<sup>2</sup>. According to H. Hands and Spicers, Ltd.<sup>3</sup>, certain chlorpropanes as penta-, hexa-, and hepta-chloropropane are suitable soluble cellulose ether flexilizing agents. They have described a method for producing films exhibiting a progressive variation in constitution, or in mechanical or physical properties between their opposite faces<sup>4</sup>, and which involves applying cellulose ether compositions in succession to a support, from which they are eventually stripped, in substantially immediate succession. A second composition is applied before any material portion of the solvent has dissipated from the composition first deposited.

Heberlein & Co.<sup>5</sup> treat cotton fibers with phosphorus oxychloride, trichloride or pentachloride in the presence of an alcoholic solution of an alkali to augment the receptivity of the fibers in dyeing, and incidentally it is an excellent pre-treatment of cellulose preliminary to etherification. This process<sup>6</sup> is also applicable to the treatment of cellulose ether fibers, whereby affinity for basic dyestuffs is materially increased. If such fibers be treated with a phos-

1. U. S. P. 1691517; abst. J. S. C. I. 1929, **48**, 15-B; Chem. Zentr. 1929, I, 2588. E. P. 261423; abst. J. S. C. I. 1928, **47**, 121-B; Chem. Zentr. 1927, I, 2358. D. R. P. 478476; abst. C. A. 1929, **23**, 4350; Chem. Zentr. 1929, II, 1351.

2. N. Grillet. U. S. P. 1571474; abst. C. A. 1926, **20**, 993; J. S. C. I. 1926, **45**, 234-B.

3. E. P. 279139; abst. C. A. 1928, **22**, 2840; J. S. C. I. 1928, **47**, 229-B; Chem. Zentr. 1928, I, 770; Kunst. 1929, **19**, 138. Can. P. 275323; abst. C. A. 1928, **22**, 1237. New Zealand P. 57726. Australia P. 5297, 1926; 15187, 1928.

4. H. Hands, U. S. P. 1666377; abst. J. S. C. I. 1928, **47**, 364-B. E. P. 281803; abst. J. S. C. I. 1928, **47**, 187-B. New Zealand P. 58031.

5. E. P. 255453; abst. J. S. C. I. 1927, **46**, 103-B; Chem. Zentr. 1927, I, 523.

6. Heberlein & Co., E. P. 261792; abst. J. S. C. I. 1927, **46**, 473-B; Silk Journal, 1927, **3**, #34, 71; Chem. Zentr. 1927, I, 2360.

phorus compound dissolved in toluene or xylene<sup>1</sup> dyestuff receptivity is enhanced.

K. Hess and H. Friese<sup>2</sup> have described a product which appears to represent an intermediate stage in the acetoysis of cellulose to cellobiose and iso-cellulose, and which upon methylation gives a hexamethylbiosan. In the ethylation of alkalicellulose with ethyl chloride<sup>3</sup>, K. Hess and A. Muller obtained only the diethyl ether, but by using ethyl sulfate and alkali as described for cellobiose formation<sup>4</sup>, triethylcellulose, melting at 255°, sintering from 240° is obtained. The products from cellulose-A (73%), viscose-cellulose (64%) and cuprammonium-cellulose (84% of theoretical yield) are chemically identical, and, unlike trimethylcellulose, insoluble in water. Pure triethylcellulose crystallizes readily from benzene, but if separation is too rapid, an amorphous powder or elastic film is obtained. Trimethylcellulose prepared from natural cellulose<sup>5</sup> after one precipitation from benzene-ligroin is readily obtained crystalline from chloroform-alcohol. If separation is too rapid the product is also amorphous or crypto-crystalline, but may be rendered crystalline by moistening with chloroform-alcohol and keeping for a few days. Crystalline trimethylcellulose gradually undergoes association in glacial acetic acid solution, the molecular weight (cryoscopically determined) increasing from about 300 to about 850 in 30 hours.

1. Heberlein & Co., E. P. 261794; abst. J. S. C. I. 1927, **46**, 552-B; Chem. Zentr. 1927, I, 2357.

2. Annalen, 1926, **450**, 40; abst. C. A. 1927, **21**, 174; J. S. C. I. 1927, **46**, 44-A; J. C. S. 1927, **132**, 44. See also K. Hess, W. Weltzein and R. Singer, Annalen, 1925, **443**, 71; abst. J. C. S. 1925, **128**, i, 641. J. Irvine and G. Robertson, J. C. S. 1926, **129**, 1488; abst. J. S. C. I. 1926, **45**, 823-A.

3. Annalen, 1927, **455**, 205; abst. C. A. 1927, **21**, 2982; J. S. C. I. 1927, **46**, 861-A; Rayon, **6**, #3, 24.

4. K. Hess and G. Salzmann, Annalen, 1925, **445**, 111; abst. J. C. S. 1925, **128**, i, 1383.

5. K. Hess and H. Pichlmayr, Annalen, 1926, **450**, 29; abst. C. A. 1927, **21**, 174; J. S. C. I. 1927, **46**, 44-A; Chem. Zentr. 1926, II, 2892.

K. Hickman<sup>1</sup> has described a daylight-loading cartridge film involving a support of light-transmitting cellulose ether or ester having on one surface a sensitive layer, and directly upon the other surface a dye layer which absorbs actinic light. In the dyeing of cellulose ethers and esters various shades of orange<sup>2</sup>, azo dyestuffs are recommended, and may be prepared by diazotizing amino derivatives of aryl sulfonylamides, then coupling the diazo-bodies with unsulfonated arylamines. As example, *m*-aminobenzenesulfonanilide is diazotized and coupled with *a*-naphthylamine; or *m*-aminobenzenesulfon-*m*-nitranilid with cresidine (*m*-amino-*p*-cresol methyl ether).

As plasticizers for cellulose esters and ethers<sup>3</sup>, halogen alkyl esters of carboxylic acids boiling above 150° (dichlorethyl and dichloropropyl carbonate as example) have been patented by the I. G. Farbenindustrie. They produce alkyl ethers of cellulose more resistant to water<sup>4</sup> by incorporating the ether with urea-formaldehyde condensates.

Cellulose ethers may be brought into a state of extreme subdivision in water<sup>5</sup>, by admixture therewith accompanied with agitation, sodium or potassium diamylnaphthylamine sulfonate, butylsulfanilate, butylaminonaphthalene sulfonate, diethylmetanilate, isopropylnaphthalenesulfonate, butylnaphthalene sulfonate or dibutylsulfanilate, a permanent emulsion being formed if agitation is continued. A cellulose ether support has been described<sup>6</sup> adapted to receive a solution of a material in an organic solvent, and used as

1. U. S. P. 1638577. E. P. 280162.

2. R. Horsfall, L. Lawrie and J. Hill, U. S. P. 1662514; abst. C. A. 1928, **22**, 1482; J. S. C. I. 1928, **47**, 296-B. E. P. 275373; abst. C. A. 1928, **22**, 2279; J. S. C. I. 1927, **46**, 776-B; Chem. Zentr. 1927, II, 2575.

3. I. G. Farbenindustrie, E. P. 257258; abst. J. S. C. I. 1928, **47**, 341-B; Chem. Zentr. 1927, I, 820.

4. I. G. Farbenindustrie, F. P. Addn. 35939 to 615876; abst. C. A. 1930, **24**, 4155.

5. *Ibid.* E. P. 264860; abst. J. S. C. I. 1928, **47**, 648-B; Chem. Zentr. 1927, II, 330.

6. *Ibid.* E. P. 279047; abst. J. S. C. I. 1928, **47**, 811-B; Chem. Zentr. 1928, I, 770. F. P. 637012.

a base for the production of films, by treatment of cellulose ether so that it is but superficially converted into regenerated cellulose.

In order to increase the solubility of cellulose ethers<sup>1</sup>, they are depolymerized with acids as hydrochloric or oxalic, or zinc chloride in hydrochloric acid, treatment of ethylcellulose with glacial acetic acid and vitriol being described. The action may take place in alcohol-benzene, wherein the ether eventually dissolves, being later precipitated by water. Cellulose ethers which do not swell in water or are soluble therein with difficulty<sup>2</sup>, are prepared from water-soluble ethers by mixing with an aqueous solution of the latter a substance which is soluble in the colloidal state in the solution, such as bakelite, latex, linseed oil, benzyl alcohol or water-insoluble ethylcellulose.

The I. G. Farbenindustrie<sup>3</sup> produce ethylcellulose by continually soaking cellulose layers with 70% NaOH at an elevated temperature in vacuo, pressing off, spreading in layers on a wire gauze and ethylating in a closed vessel at 100° with ethyl chloride under 5 atmospheres pressure; and manufacture methylcellulose with 60% NaOH, by pressing, then rolling with a wire gauze on a drum, and finally etherifying with methyl chloride under 5 ats. pressure at 70°. As a plasticizer for cellulose derivatives, di-*n*-butyl phthalate has been brought forward<sup>4</sup>, as well as diamyl and isoamyl phthalate for the same purpose<sup>5</sup>. Ethylcellulose 10, isoamyl phthalate 10-12 parts gives a syrupy, homogen-

1. I. G. Farbenindustrie, E. P. 277111; abst. C. A. 1928, **22**, 2464; J. S. C. I. 1927, **46**, 860-8; Plastics 1928, **4**, 508; Chem. Zentr. 1928, I, 445.

2. *Ibid.* E. P. 252176; abst. C. A. 1927, **21**, 1548; J. S. C. I. 1928, **47**, 154-B; Chem. Zentr. 1927, I, 1091; Kunst. 1929, **19**, 90. F. P. 615876.

3. E. P. 275660; abst. C. A. 1928, **22**, 2464; J. S. C. I. 1929, **48**, 50-B; Plastics, 1928, **4**, 508; Chem. Zentr. 1927, II, 2583. F. P. 639150; abst. C. A. 1929, **23**, 703-B.

4. *Ibid.* E. P. 245469; abst. Chem. Zentr. 1926, I, 2988. See D. R. P. 127816.

5. *Ibid.* E. P. 252328; abst. C. A. 1927, **21**, 1548; Chem. Zentr. 1927, I, 667.

eous paste. Diphenyl phthalate and cresyl phthalate<sup>1</sup> have already been patented for use as a camphor substitute in the celluloid industry. As a plasticizing group for cellulose acetates<sup>2</sup> or cellulose ethers<sup>3</sup>, ethyleneglycol monomethyl ether or monoethyl ether and the corresponding propyl and butyl ethers have been accorded some prominence. 1,4-Dioxane has received patent protection as a cellulose ether solvent<sup>4</sup> and desirable wetting material for fibrous substances<sup>5</sup>.

Valuable emulsifying agents are claimed to result by employing organic sulfonic acids or their salts in conjunction with alkylcelluloses, especially dimethylcellulose<sup>6</sup>, the sodium salts of isopropyl-, butyl- and benzyl-naphthalene-sulfonates and butylnaphthalene sulfonic acid being specifically claimed. As a softener for the cellulose esters and ethers<sup>7</sup>, or as "water-swelling substances," oily or resinous combinations have been patented, obtained by prolonged heating of urea, thiourea or urethane with ethyl or benzyl alcohol, butylene glycol, glycerol, acetophenone or the cyclic acetal produced by treating glycerol with acetic acid.

As suitable for the back layer of a photographic film to prevent curling, mixed cellulose esters and ester-ethers are advocated, such as cellulose acetate-stearate, ethylcel-

1. Farbwerke, vorm. Meister, Lucius & Brüning, D. R. P. 127816; abst. Wag. Jahr. 1902, II, 594; Bied. Tech. Chem. Jahr. 1901-2, **24**, 601; Chem. Zentr. 1902, I, 288; Chem. Ztg. (Jan.-June) 1902, **26**, 189; Zts. Ang. 1902, **15**, 114; Jahr. Chem. 1902, **55**, 1056; Mon. Sci. 1902, **58**, 78.

2. I. G. Farbenindustrie, E. P. 278735; abst. J. S. C. I. 1928, **47**, 155-B; Chem. Zentr. 1928, I, 1824; Kunst. 1929, **19**, 113.

3. *Ibid.* E. P. 251303; abst. J. S. C. I. 1928, **47**, 155-B; Chem. Zentr. 1928, I, 1824; Kunst. 1929, **19**, 90.

4. *Ibid.* E. P. 275653; abst. J. S. C. I. 1927, **46**, 905-B; C. A. 1928, **22**, 2464; Chem. Zentr. 1927, II, 2583.

5. *Ibid.* E. P. 245098; abst. C. A. 1927, **21**, 292; J. S. C. I. 1928, **47**, 154-B. A. Knorr, D. R. P. 431249; abst. J. S. C. I. 1927, **46**, 249-B; Chem. Zentr. 1926, II, 228.

6. *Ibid.* E. P. 268387; abst. C. A. 1928, **22**, 1484; J. S. C. I. 1928, **47**, 152-B; Chem. Zentr. 1927, II, 1908. Compare E. P. 258551; abst. C. A. 1927, **21**, 3095.

7. *Ibid.* E. P. 278390; abst. C. A. 1928, **22**, 2673; J. S. C. I. 1928, **47**, 648-B; Chem. Zentr. 1928, I, 864. Cites E. P. 209697, A. Alexander; abst. C. A. 1924, **18**, 1759; J. S. C. I. 1924, **43**, 224-B.

lulose stearate, ethylcellulose phosphate or cellulose acetate-phosphate<sup>1</sup>. They are obtainable by acting upon a cellulose ether or cellulose ester with free hydroxyl groups, with stearyl chloride or phosphorus oxychloride in the presence of an organic solvent; for example, ether or benzine in the treatment of ethylcellulose.

In the dyeing of cellulose ethers or esters<sup>2</sup>, yellowish-brown to brown shades are producable by the use of primary disazo-dyestuffs, obtained by coupling a mono- or dihydroxy compound of the benzene or naphthalene series with 2 molecules of diazo compounds, provided that the final product contains at least one free or substituted amino-group, not more than one sulfonic group, and not more than one naphthalene nucleus. Examples are phenol-*m*-phenylenediamine-sulfanilic acid (yellow) and resorcinol-, which gives orange to brown dyes. Or<sup>3</sup>, the cellulose ether may be colored by monoazo dyes containing as coupling component an *o*-aminophenol ether or monoacyl-*m*-phenylenediamine. Yellow is produced from the dye prepared from 2-chloraniline-5-sulfonic acid and 3-amino-4-cresol methyl ether. Another series of azo dyes which produce intense shades on cellulose ethers and esters<sup>4</sup>, are made by coupling a diazo compound of the benzene or naphthalene series such as diazotized *p*-aminoacetanilide, diazotized *p*-nitraniline or chloraniline with a *p*-substituted phenol as *p*-cresol, *p*-acetaminophenol or *m*-amino-*p*-cresol.

1. I. G. Farbenindustrie, E. P. 270347; abst. C. A. 1928, **22**, 1552; J. S. C. I. 1927, **46**, 893-B; Chem. Zentr. 1927, II, 1324. F. P. 635281.

2. *Ibid.* E. P. 258611; abst. C. A. 1927, **21**, 3134; J. S. C. I. 1927, **46**, 874-B; Chem. Zentr. 1927, I, 1215. Ital. P. 254352.

3. *Ibid.* E. P. 245790; abst. C. A. 1927, **21**, 502; J. S. C. I. 1927, **46**, 438-B; Chem. Zentr. 1926, II, 649. H. Eichwede, E. Fischer and C. Müller, U. S. P. 1692492, 1692493; abst. C. A. 1929, **23**, 718; J. S. C. I. 1929, **48**, 430-B; Chem. Zentr. 1929, II, 1852.

4. *Ibid.* E. P. 270351; abst. C. A. 1928, **22**, 1692; Chem. Zentr. 1927, II, 1094. Cf. E. P. 269918; abst. C. A. 1928, **22**, 1480.

In printing on cellulose ethers or esters with vat dye-stuffs<sup>1</sup>, especially as applied to pile fabrics, the material is first printed with a dye thickened with a solution of cellulose ether, then treated with a reducing agent and an alkali and steamed, water-soluble cellulose ethers being advocated as suitable. Unsulfonated *p*-arylamino-diphenylamines, carrying in one terminal nucleus three *o*- and *p*-substituents two of which are nitro groups, and a carboxyl group either in the other of the three positions or in the middle nucleus, give brown shades on acetate silk or cellulose ether filaments. Examples are: 2,6-dinitro-4'-anilinodiphenylamine-4-carboxylic acid, 2,4-dinitro-4'-anilinodiphenylamine-6-carboxylic acid, 2,4-dinitro-4'-*p*-hydroxyanilino-6-methyldiphenylamine-3'-carboxylic acid, 2,6-dinitro-4'-*b*-anisidinodiphenylamine-4-carboxylic acid, and methyl-2,6-dinitro-4'-anilino-3'-carboxyldiphenylamine-4-carboxylate<sup>2</sup>.

In the formation of water-soluble dinitroarylamino-diarylamines<sup>3</sup> as cellulose ether and ester dyestuffs, *p*-aminodiphenylamine or one of its substitution products is condensed with an aromatic dinitrohalogen compound, as 3,5-dinitro-4-chlorbenzoic acid or one of its salts, 2-chlor-3,5-dinitrobenzoic acid or similar compounds. Insoluble or difficultly soluble dyes are preserved in a state of fine subdivision<sup>4</sup>, by incorporating methylcellulose with them, which addition may be made during or after the manufacture of the dye. This firm has also found<sup>5</sup> that the

1. I. G. Farbenindustrie, E. P. 279864; abst. C. A. 1928, **22**, 3051; J. S. C. I. 1929, **48**, 15-B; Chem. Zentr. 1928, I, 1094. F. P. 642991; abst. C. A. 1929, **23**, 1514. F. P. Addn. 37282 to 642991; abst. C. A. 1931, **25**, 2576. D. R. P. 495712.

2. *Ibid.* E. P. 279135; abst. C. A. 1928, **22**, 2847; J. S. C. I. 1929, **48**, 320-B; Chem. Zentr. 1928, I, 755.

3. *Ibid.* E. P. 279133; abst. C. A. 1928, **22**, 2847; J. S. C. I. 1928, **47**, 516-B; Chem. Zentr. 1928, I, 756. F. P. 641832; abst. C. A. 1929, **23**, 1277.

4. *Ibid.* E. P. 269918; abst. C. A. 1928, **22**, 1480; J. S. C. I. 1928, **47**, 666-B; Chem. Zentr. 1927, II, 1096.

5. *Ibid.* E. P. 272482; abst. C. A. 1928, **22**, 1859; J. S. C. I. 1928, **47**, 744-B; Chem. Zentr. 1927, II, 2232. Patent cites E. P. 272469; J. S. C. I. 1928, **47**, 598-B; Chem. Zentr. 1927, II, 2120. E. P.

ethers of 1,4-diamino-2-hydroxyanthraquinones produce brilliant red to blue shades on cellulose ethers and esters. 2-Ethoxy-1,4-diaminoanthraquinone acts similarly.

Dyeings on cellulose ethers are obtainable by using monosulfonated aryl-azo-diarylamines containing at least one nitro-group in the diarylamine complex. 4-Benzeneazo-2',6'-dinitro-4'-sulfodiphenylamine gives brown or green tints, while 4-benzeneazo-4'-nitro-2'-sulfodiphenylamine dyes yellow<sup>1</sup>.

The I. G. Farbenindustrie<sup>2</sup> have described a series of mixed cellulose esters and ester-ethers obtained by treating the cellulose ether or ester with an inorganic acid chloride in the presence of an acid binding agent (other than pyridine) such as an organic base, ammonia, magnesia or a carbonate. Radicals of silicic, phosphoric, phosphorous, sulfuric or antimonous acid may be introduced, and by the use of mixed acid anhydrides as boroacetic anhydride or lauric-myristic acid, corresponding esters result. Specific directions are given for the production of cellulose boroacetate, lauro-myristate, nitrobenzoate, aceto-stearate, and ethylcellulose silicate, ethylcellulose myristate and ethylcellulose benzoate.

Crude benzylcellulose may be purified by malaxating with a water-soluble salt<sup>3</sup>, then extracting the benzyl alcohol and benzyl chloride by benzene, acetone or alcohol,

211720; abst. C. A. 1924, **18**, 1914; J. S. C. I. 1924, **43**, 375-B; Ann. Rep. S. C. I. 1924, **9**, 139; *Faser*. 1924, **6**, 107; *Chem. Zentr.* 1924, II, 2500. F. P. 635054.

1. I. G. Farbenindustrie, as in English Patent 275230; abstract *Chemical Abstracts* 1928, **22**, 2279; J. S. C. I. 1928, **47**, 783-B; *Chem. Zentr.* 1927, II, 2715. French Patent 638138; abstract *Chem. Abst.* 1929, **23**, 285. U. S. P. 1674168; abst. C. A. 1928, **22**, 2847; J. S. C. I. 1928, **47**, 774-B; *Chem. Zentr.* 1928, II, 1944. D. R. P. 468981; abst. C. A. 1929, **23**, 994.

2. E. P. 300942; abst. C. A. 1929, **23**, 4071; J. S. C. I. 1929, **48**, 126-B. Addn. 34859 to F. P. 629861; abst. C. A. 1930, **24**, 1216. Cites D. R. P. 332203; F. P. 581160; E. P. 219926.

3. U. S. P. 1771529; abst. C. A. 1930, **24**, 4631; J. S. C. I. 1930, **49**, 901-B; *Plastics*, 1930, **6**, #10, 608. E. P. 265491; abst. J. S. C. I. 1927, **46**, 296-B; C. A. 1928, **22**, 317; *Chem. Zentr.* 1927, I, 3162. D. R. P. 522170; abst. C. A. 1931, **25**, 3187. Compare U. S. P. 1751685; abst. C. A. 1930, **24**, 2599.



and finally washing the extracted product with water. In the dyeing of benzylcellulose<sup>1</sup>, Malachite green, Chrome-blue BMJ, Azoyellow or dianisidine with ammonium chloride, sulfate or acetate has been disclosed.

In the preparation of sulfonated cellulose derivatives by causing cellulose to react in the presence of an alkaline agent with an arylhalidesulfonic acid or salt<sup>2</sup>, benzylcellulose sulfonate, aluminum benzylsulfonate, sodium benzylchloride-sulfonate, sodium benzyl-chloride *p*-sulfonate and sodium xylylchloride-sulfonate have been specified. In the formation of aminocellulose compounds<sup>3</sup>, alkalicellulose is treated with benzenesulfochloride; or cellulose toluene-4-sulfonate with diethylamine, or with pyridine and benzoyl chloride or with isoamylamine, acetylation or ethylation completing the process. Ethylaminocellulose toluene-4-sulfonate is an example of a compound produced<sup>4</sup>.

According to J. Irvine and J. MacDonald<sup>5</sup>, in the methylation of starch with methyl sulfate (3 times) followed by methyl iodide and silver oxide, there first results a dimethylstarch (32.7% methoxyl) which gives no color with iodine and which on hydrolysis yields a dimethylmethylglucoside. Further treatment with methyl sulfate (4 times) gives a "methylated starch" in which 7 of the 9 OH groups are methylated (36.2% methoxyl). With 24 methylations a trimethylstarch results (43.75% methoxyl), giving on hydrolysis trimethylmethylglucoside and on further hydrolysis only 2,3,6-trimethylglucose.

1. I. G. Farbenindustrie, D. R. P. 453215 Addn. to 438378; abst. Chem. Zentr. 1928, I, 754; Die Kunstseide, 1928, #1, 16.

2. *Ibid.* E. P. 277317; abst. J. S. C. I. 1928, **47**, 853-B; Chem. Zentr. 1928, I, 445. U. S. P. 1682382; abst. J. S. C. I. 1929, **48**, 14-B. F. P. 640687.

3. *Ibid.* F. P. 641043; abst. C. A. 1929, **23**, 1266; Chem. Zentr. 1929, I, 2925. C. Briggs, Z. angew.Chem. 1913, **26**, 255; abst. C. A. 1913, **7**, 2855; J. S. C. I. 1913, **32**, 595. P. Karrer and W. Wehrli, Helvetica Chim. Acta, 1926, **9**, 591; abst. C. A. 1926, **20**, 3819. Compare F. P. 639150; abst. C. A. 1929, **23**, 703.

4. *Ibid.* E. P. 279801; abst. J. S. C. I. 1929, **48**, 167-B; Silk Journal, 1928, **4**, #46, 68; Chem. Zentr. 1928, I, 977.

5. J. Chem. Soc. 1926, **129**, 1502; abst. C. A. 1926, **20**, 2830; Chem. Zentr. 1926, II, 1265.

Cellulose ethers from aromatic sulfonic acids<sup>1</sup> and naphthene ethers<sup>2</sup> have been described, and obtained by treating alkal cellulose with *p*-toluenesulfonyl chloride, or benzenesulfonyl chloride. A. Knorr<sup>3</sup> has received patent protection for the use of dioxane in conjunction with dibutyl phthalate, methylcyclohexanone, methylglycol acetate and similar bodies as a solvent for nitro-, acetyl-, lauryl- and ethyl-cellulose. A compound solvent of nitromethane with methyl-, ethyl-, propyl-, butyl or amyl alcohol has been put forward by L. Lilienfeld<sup>4</sup>, said to be especially useful with water-insoluble ethylcellulose.

In the preparation of cellulose thiourethanes<sup>5</sup>, as starting material any cellulose derivative other than cellulose xanthofatty acid is used that contains the group CSS, the product being treated with dimethyl or diethyl sulfates or with ethyl bromide or iodide, and then with aniline, toluidine, aminophenol, or benzylamine. After neutralization with acetic acid, the product is reacted upon with ethyl chlorcarbonate, then with aniline or similar bodies. The products formed are soluble in dilute alkalis, and in some cases in pyridine. Or<sup>6</sup>, for the precipitation of the cellulose urethane, a strong acid as 25-65% sulfuric acid, 45-70% phosphoric acid, 20-35% hydrochloric acid or strong acetic acid may be used. Arylestere of cellulose xanthic acid have

1. G. Kita, T. Nakashima and I. Sakurada, *Cell. Ind.*, Tokio, 1926, **2**, 405; *abst. Caout. et Gutta.* 1927, **24**, 13640; *Chem. Zentr.* 1927, **I**, 1429.

2. G. Kita, T. Mazume, T. Nakashima and I. Sakurada, *Cell. Ind.*, Tokio, 1926, **2**, 31; *abst. Caout. et Gutta.* 1927, **24**, 13424. *Kunststoffe*, 1926, **16**, 41; *abst. C. A.* 1926, **20**, 3079. *Kunststoffe*, 1926, **16**, 69; *abst. C. A.* 1926, **20**, 3079.

3. U. S. P. 1780883; *abst. C. A.* 1931, **25**, 223; *J. S. C. I.* 1930, **49**, 1164-B. E. P. 275653; *abst. J. S. C. I.* 1927, **46**, 905-B; *C. A.* 1928, **22**, 2464; *Chem. Zentr.* 1927, **II**, 2583. See also E. P. 245098; *F. P.* 688315.

4. U. S. P. 1599569; *abst. C. A.* 1926, **20**, 3567; *J. S. C. I.* 1926, **45**, 1010-B; *Ann. Rep. S. C. I.* 1926, **II**, 131, 368; *Rev. Gen. Mat. Plast.* 1927, **#1**, 46; *Chem. Zentr.* 1927, **II**, 380.

5. L. Lilienfeld, E. P. 248246; *abst. J. S. C. I.* 1926, **45**, 400-B; *Chem. Zentr.* 1926, **II**, 2513. D. R. P. 526197.

6. E. P. 248994; *abst. J. S. C. I.* 1926, **45**, 532-B; *Chem. Zentr.* 1926, **II**, 2514. U. S. P. 1674404; *abst. J. S. C. I.* 1928, **47**, 853-B.

been described<sup>1</sup>, the methyl and ethyl esters being white powders soluble in dilute alkalis to a clear viscous solution suitable for film, filament and plastics formation.

For the formation of films<sup>2</sup> a 6-10% solution of an alkali-soluble phenylthiourethane (cellulose xanthogenateanilid), xylyl-, tolyl-, or ethyl-thiourethane is dissolved in 10% NaOH, and the solution either spread on a glass surface by hand or on an endless surface by machine. After the film has solidified dilute acid is added to neutralize the alkali present and thereby coagulate the film which precipitates in a transparent condition.

In an investigation of the relation of trimethylglucose to the constitution of cellulose, F. Micheel and K. Hess<sup>3</sup>, found that methylation of trimethylmethylglucoside obtained from trimethylcellulose gave a mixture of tetramethylglucosides. They prepare trimethylcellulose in the crystalline condition by concentration of 10% solutions in 50% ethyl alcohol-chloroform mixture.

C. Muller<sup>4</sup> has added to the classes of dyestuffs suitable for coloring the cellulose ethers and esters, obtaining a deep violet tint by the use of 1,4-diaminoanthraquinone-2-sulfonic acid, a green hue with 1-phenylamino-4-amino-7-chloranthraquinone-3-sulfonic acid, and reddish-violet with 4-oxy-1-aminoanthraquinone-3-sulfonic acid. M. Ow-Eschingen<sup>5</sup> in a process for augmenting the electric disruption strength resistance of cellulose ether and ester films, finds the dielectric character of the films is increased by soaking them with an oil of high disruptive strength (e.g. paraffin oil or transformer oil), the process being carried

1. E. P. 252654; abst. J. S. C. I. 1926, **45**, 1009-B; Chem. Zentr. 1927, I, 1090.

2. Aust. P. 108400.

3. Annalen, 1926, **449**, 146; abst. C. A. 1927, **21**, 173; J. C. S. 1926, **129**, A. 1230; Chem. Zentr. 1926, II, 2890.

4. U. S. P. 1587669; abst. C. A. 1926, **20**, 2588; J. S. C. I. 1926, **45**, 628-B; Plastics, 1926, Oct. 368; Chem. Zentr. 1927, I, 185. See also E. P. 228557.

5. E. P. 281663; abst. C. A. 1928, **22**, 3528; J. S. C. I. 1928, **47**, 824-B; Chem. Zentr. 1928, I, 1600.

out in vacuo and subsequently under a pressure above atmospheric.

Pathe Cinema<sup>1</sup> prepare filaments obtained from cellulose ethers by coagulation in a polished and transparent condition without further treatment, by employing for the preparation of the solution an anhydrous solvent as dry acetone. They prepare plastic masses with ethyl- or benzyl-cellulose<sup>2</sup>, by means of the phosphates of monomethyl-diphenyl, monoethyl-diphenyl, dimethyl-monophenyl or diethyl-monophenyl, or in the above, substituting the cresyl radical for phenyl, in amount about 20% on the weight of the cellulose ether. They have also advocated the use for the same purpose<sup>3</sup> of trichlorethyl phosphate in conjunction with hexachlorethane, hexachlorbenzene and dicresylglyceryl ether, especially in conjunction with benzylcellulose. They prepare films<sup>4</sup> by spreading a solution of cellulose ether on a smooth surface, coagulating, drying, then bringing back the transparency by means of a solvent in the liquid condition or vapor phase.

D. Peacock<sup>5</sup> has described the application of nitrobenzylcelluloses to the dyeing of cotton, the latter being dyed in shades fast to washing by treatment with *m*- or *p*-nitrobenzylphenylmethylammonium chloride, subsequent reduction of the nitro-group, then diazotization and subsequent coupling with suitable components as *b*-naphthol. In coating sheets of cellulose ethers, especially for electric condensers, E. Pffner<sup>6</sup>, finds that a metal coating is ren-

1. E. P. 267112; abst. C. A. 1928, **22**, 1237; Chem. Zentr. 1927, II, 352. F. P. 624278; abst. J. S. C. I. 1928, **47**, 744-B; Chem. Zentr. 1927, II, 2025.

2. F. P. 606969; abst. J. S. C. I. 1927, **46**, 552-B; Chem. Zentr. 1927, I, 1091; Kunst. 1926, **16**, 207.

3. F. P. 612414; abst. J. S. C. I. 1927, **46**, 406-B; Chem. Zentr. 1927, I, 380.

4. E. P. 247974; abst. C. A. 1927, **21**, 649; Chem. Zentr. 1926, I, 3370. F. P. 606543.

5. J. Soc. Dyers & Col. 1926, **42**, 53; abst. C. A. 1926, **20**, 1325; J. S. C. I. 1926, **45**, 270-B; Chem. Zentr. 1926, I, 3102.

6. E. P. 261392; abst. C. A. 1927, **21**, 3461; Chem. Zentr. 1927, I, 1911.

dered adherent by colloiddally depositing an intermediate layer of metal or metallic oxide.

For the preparation of dielectric films of cellulose ethers E. Pfiffner<sup>1</sup> superposes cellulose ether or ester films before they have completely hardened, so that they may be coated by pressure and heat without passage of any impurities from one film to another. In the dyeing of cellulose esters or ethylcellulose<sup>2</sup>, the material is first mordanted with a 40-55% solution of a ferric salt at 40-60° and then dyed with logwood or other vegetable dyes. I. Sakurada and T. Nakashima<sup>3</sup>, as the result of their investigations, have come to the conclusion that P. Karrer and T. Lieser<sup>4</sup> in their work on methylation of viscose and the preparation of methylhydrocellulose soluble in water, obtained a methylcellulose rather than the methyl ester of xanthogenic acid (methyl xanthogenate).

F. Schmidt<sup>5</sup> produces moldable products as celluloid substitutes by combining cellulose ethers with such albuminous bodies as casein and gelatin. Films and fabrics are coated, according to one process<sup>6</sup>, by forming two layers of cellulose derivative, one of a cellulose ester and on this a cellulose ether layer is superposed, or conversely, using a solvent for dissolving the product of the upper layer which is a non-solvent of the cellulose compound constituting the bottom layer. P. Seel lowers the viscosity characteristics of ethylcellulose by making a solution of faint acidity, and then incubating this at about 65° until the viscosity has

1. E. P. 267917; abst. C. A. 1928, **22**, 1237; Chem. Zentr. 1927, II, 521; Kunst. 1929, **19**, 112.

2. G. Rivat, E. Cadgene and C. Dreyfus, U. S. P. 1779494; abst. C. A. 1931, **25**, 217; J. S. C. I. 1930, **49**, 1149-B. E. P. 273692; abst. C. A. 1928, **22**, 2067; J. S. C. I. 1928, **47**, 744-B; Chem. Zentr. 1927, II, 2573. F. P. 636057; abst. C. A. 1928, **22**, 4835.

3. Sci. Papers Inst. Phys. Chem. Research (Tokyo) 1927, **6**, 197; abst. C. A. 1928, **22**, 683.

4. Cellulosechemie 1926, **7**, 1; abst. C. A. 1926, **20**, 1515.

5. F. P. 612937; abst. Caout. et Gutta. 1927, **24**, 13534; Chem. Zentr. 1927, I, 1092. D. R. P. 73377; abst. Jahr. Chem. 1894, **47**, 1632; Wag. Jahr. 1894, **40**, 637.

6. G. Schneider and C. Dreyfus, E. P. 274841; abst. C. A. 1928, **22**, 2273; J. S. C. I. 1928, **47**, 782-B; Chem. Zentr. 1927, II, 2788.

been reduced to the point desired<sup>1</sup>. W. Segal<sup>2</sup> has detailed the versatility of the cellulose ethers in the arts and indulged in some prognostications as to their future development.

In the electrodeposition of cellulose ether or acetate<sup>3</sup>, the surface is first rendered electroconductive, and then coated with a layer of colloidal material permeable to the dispersion medium of the emulsion of the cellulose derivative prior to the electrodeposition of the emulsion. A reducing agent as sodium or ammonium sulfite, thiosulfate or hyposulfite, resorcinol or hydroquinone<sup>4</sup> may be added to the emulsion used for electrodeposition to reduce oxygen formation in the anode zone. An emulsion of rubber and cellulose ethers which may be deposited together<sup>5</sup>, has also been described. In a preferred method for carrying the invention into effect<sup>6</sup>, the rubber and cellulose ether are dissolved separately in benzene and then combined. It is claimed that any ratio of rubber to cellulose ether is electrodepositable.

Cables for use under relatively high temperature conditions have been described comprising a stranded conductor encased in a sheath of ethylcellulose<sup>7</sup>. Cellulose ethers may be colored by adding to their solutions a metallic salt in solution, which gives a precipitate by means of double decomposition. Ferric chloride dissolved in a cellu-

1. U. S. P. 1635013; abst. C. A. 1927, **21**, 2985; J. S. C. I. 1927, **46**, 774-B; Plastics, 1927, **3**, #11, 608; Chem. Zentr. 1927, II, 2025. See also U. S. P. 1548938, 1679903.

2. Plastics, 1926, **2**, #4, 120.

3. Kodak, Ltd., S. Sheppard and C. Beal, E. P. 251271; abst. J. S. C. I. 1927, **46**, 850-B; Chem. Zentr. 1926, II, 3080.

4. S. Sheppard and L. Eberlin, U. S. P. 1580795; abst. J. S. C. I. 1926, **45**, 639-B; Ann. Rep. S. C. I. 1926, **11**, 400; Chem. Zentr. 1926, II, 501. E. P. 253085; abst. J. S. C. I. 1927, **46**, 82-B; Chem. Zentr. 1926, II, 1796. E. P. 253091; abst. Chem. Zentr. 1926, II, 1796. Compare U. S. P. 1476374, 1580795, 1583704, 1589326, 1589327, 1589328, 1589329, 1589330, 1589331, 1589332. E. P. 251979, 261700.

5. U. S. P. 1589330; abst. J. S. C. I. 1926, **45**, 794-B; Chem. Zentr. 1926, II, 1344.

6. U. S. P. 1589332; abst. J. S. C. I. 1926, **45**, 794-B; Chem. Zentr. 1926, II, 1344.

7. Siemens-Schuckertwerke A. G., E. P. 281333.

lose ether solution and treated with potassium ferrocyanide would be a familiar example<sup>1</sup>. In the production of powdered plastic material<sup>2</sup>, finely powdered fillers and coloring agents are suspended in a solution of a cellulose ester or ether and the whole precipitated, as by the addition of water. The cellulose ether solvent used should be without solvent action on the fillers. After separation, washing and drying the product, it is molded by heat and pressure. Plastic masses are producible by the use of hydrates or ether-hydrates of cellulose<sup>3</sup>, in conjunction with deliquescent bodies as antiseptic preparations.

Deep black shades of excellent fastness are producible on cellulose ether and ester fabrics and filaments<sup>4</sup>, by means of a diaminoazo dye (e.g. hydrolyzed *p*-aminoacetanilide with cresidine) in presence of a dispersing agent, and then diazotized and developed in weak acid medium with 2,3-hydroxynaphthoic acid or *b*-naphthol. Navy blue shades are obtained by using less diaminoazo compound. In the production of artificial yarns and threads of cellulose ethers<sup>5</sup>, the Societe pour la Fabrication de la Soie Rhodiaseta have evolved a method of coloring various kinds of yarn for the purpose of distinguishing them. They have also described a method for producing cellulose ether or

1. Soc. Chim. Des Usines du Rhone, E. P. 275553; abst. C. A. 1928, **22**, 2279; J. S. C. I. 1928, **47**, 639-B. F. P. 619764; abst. J. S. C. I. 1928, **47**, 188; Chem. Zentr. 1927, II, 765. F. Addn. 33001.

2. Soc. Chim. des Usines du Rhone, E. P. 275558; abst. C. A. 1928, **22**, 2272; J. S. C. I. 1928, **47**, 330-B. F. P. Addn. 33066 to 622733; abst. C. A. 1929, **23**, 1267; Plastics, 1929, **5**, 390. F. P. 622733; abst. Chem. Zentr. 1927, II, 1221. Compare F. P. 520101, 569642. E. P. 147904.

3. Soc. Francaise des Crins Artificiele, Aust. P. 104713. Same as E. P. 224487; abst. C. A. 1925, **19**, 1348; J. S. C. I. 1925, **44**, 126-B; Chem. Zentr. 1925, I, 1256. D. R. P. 401449; abst. Chem. Zentr. 1924, II, 2303; Kunst. 1925, **15**, 12.

4. Soc. Chem. Ind. in Basle, E. P. 281704; abst. J. S. C. I. 1928, **47**, 521-B; Chem. Zentr. 1928, I, 1717.

5. E. P. 251580; abst. J. S. C. I. 1926, **45**, 975-B; Rev. Gen. Mat. Plast. 1927, #1, 45; Chem. Zentr. 1927, I, 1251. D. R. P. 480899; abst. C. A. 1929, **23**, 5048; Chem. Zentr. 1929, II, 1993. F. P. 597394; abst. Chem. Zentr. 1926, I, 1743. Swiss P. 123891; abst. Chem. Zentr. 1928, I, 2147. Swiss P. 131327.

ester filaments<sup>1</sup> by the dry-spinning process, by a method permitting rounded or star-shape outline filaments to be obtained. A similar process is that of Spicers, Ltd.<sup>2</sup>

In an investigation of the structure of ramie cellulose as derived from X-ray data, O. Sponsler and W. Dore<sup>3</sup> find that the cellulose structure is stabilized longitudinally by the primary valence forces uniting the glucose units, and laterally by the secondary valence forces of the oxygen atoms, this proposed structure accounting for the longitudinal tensile strength, and for the difference in longitudinal and lateral expansion, the OH groups on C atoms 2, 3 and 6 being open to substitution, which agrees with Irvine's cellulose ethylation data.

E. de Stubner<sup>4</sup> has described a process for pigment manufacture in which the pigment in an aqueous medium is precipitated upon a soluble cellulose derivative as cellulose ether, then dehydrating the product by washing with a non-aqueous, water-miscible liquid compatible with the product to be pigmented, until the water in the mixture has been replaced by the latter liquid. E. Teupel<sup>5</sup> claims to produce cellulose ethers in a more rapid and economical manner by replacing the alkali hydroxide by a 25-40% alkali hydroxide solution containing salt.

H. Urban<sup>6</sup> has published details with analyses upon the methylation of lignin, cellulose and wood. On methylation of lignin, the methoxyl content rose rapidly from 15% to 24% and finally to 32%. Cellulose readily methylated to 44.5%, and wood to 40.9%. From this, on treatment with

1. E. P. 248696; abst. J. S. C. I. 1926, **45**, 945-B. U. S. P. 1583475. F. P. 598081.

2. Ital. P. 254524. India P. 12788, 1926.

3. Fourth Colloid Symposium Monograph, 1926, 174; abst. C. A. 1927, **21**, 3268; Chem. Zentr. 1928, II, 2527.

4. E. P. 277949; abst. J. S. C. I. 1929, **48**, 365-B; Chem. Zentr. 1928, I, 266.

5. D. R. P. 435346; abst. J. S. C. I. 1927, **46**, 388-B; Chem. Zentr. 1927, I, 207. Addn. to D. R. P. 408342; abst. J. S. C. I. 1925, **44**, 397-B. See p. 98, note 10.

6. Cellulosechemie, 1926, **7**, 73; abst. C. A. 1926, **20**, 3080.



HCl-phosphoric acid, a methylignin of about 25% methoxyl was obtained which was further methylated to 32%. W. Webb<sup>1</sup> has described a film which maintains its flexibility after prolonged heating to 65°, comprising colloidized water-insoluble ethylcellulose having an inorganic alkali distributed therein to an alkalinity in excess of pH 7. In the purification, decomposition and stabilization of cellulose ethers<sup>2</sup>, the material is cooked with water under atmospheric pressure, steamed, or subjected to the action of a vacuum at ordinary temperature or with heating.

In the coloring of lacquers composed of cellulose ethers<sup>3</sup>, basic dyestuffs which have the property of forming lakes with complex acids or salts, are dissolved in the lacquer, and a solution of such acids (phosphotungstic, phosphomolybdic, silicotungstic, phosphotungstomolybdic) added to induce precipitation in a very fine state of subdivision. Cellulose ethers may be dyed with azo colors obtained by combining an acid-substituted aromatic nitro-diazo-compound with an aromatic amine. Examples, 4-nitro-1-benzoate of soda-2-azomethylbenzylaniline (orange shades), 2-nitro-4-sulfobenzene-1-azoethyl-*b*-naphthylamine (bluish-pink)<sup>4</sup>. A laminated film particularly useful in photography<sup>5</sup> comprises a layer of polymerized vinyl chloride with layers of a cellulose ether or ester. By reason of a co-operating anti-static layer or layers, the film is said to be free from electrification or "static" effects. In order to increase the absorption of cellulose ethers and esters for chemical or tinctorial bodies, the filament, film or textile is first treated with ammonium cyanate or isothiocyanate, then

1. U. S. P. 1583709; abst. C. A. 1926, **20**, 2073; J. S. C. I. 1926, **45**, 580-B; Plastics, 1926, **2**, 453; Chem. Zentr. 1926, II, 957.

2. Wolff & Co. and H. Schulz, D. R. P. 440844; abst. J. S. C. I. 1927, **46**, 811-B; Chem. Zentr. 1927, I, 2028. D. R. P. 511020; abst. C. A. 1931, **25**, 1379; Chim. et Ind. 1931, **25**, 1218.

3. I. G. Farbenindustrie, A. G., E. P. 275969.

4. W. Duisberg and W. Hentrich, U. S. P. 1575324; abst. C. A. 1926, **20**, 1528.

5. R. Stinchfield, U. S. P. 1627935. See P. Seel, U. S. P. 1431900.

with urea, urethanes, thiourea, thiourethanes or guanidine<sup>1</sup>.

C. Ellis has disclosed a method of covering automobile bodies and similar surfaces<sup>2</sup> by combining a synthetic resin with nitrocellulose or a cellulose ether to which urea or magnesium lactate as stabilizers are added, the ether and resin being dissolved in a combined volatile and slowly evaporative solvent. In order to diminish the inflammability of cellulose composition in general<sup>3</sup> it has been found that compositions which permit of a self sustaining combustion by the application of a flame at ordinary temperature, may be prevented from burning under normal temperature, provided there is present a heat absorbing compound capable of taking up through decomposition or volatilization, the major part of the heat that would be necessary to raise the components to the point at which ignition can be sustained. The cellulose ethers have been patented as such an exothermic substance, used either alone, or in conjunction with cerium oxalate or carbonate<sup>4</sup>.

In treating textiles<sup>5</sup> composed primarily of cellulose ethers, a silky gloss and an elastic finish or feel is imparted by treatment with a halohydrin in the presence of an alkali. *α*-Monochlorhydrin, epichlorhydrin and ethylenechlorhydrin with sodium hydroxide are said to give best results. As solvents for cellulose xanthogenate (xanthate) and which combine with cellulose to form new compounds, have been disclosed monomethylaniline<sup>6</sup>, monoethyltoluidine and monomethylxylylidine.

1. H. Dreyfus, F. P. 34391 Addn. to F. P. 634165; abst. C. A. 1929, **23**, 4581.

2. U. S. P. 1529056; abst. C. A. 1925, **19**, 1502.

3. W. Lindsay, U. S. P. 1538859; abst. Chem. Zentr. 1925, IV, 1322. See U. S. P. 1538861.

4. *Ibid.* U. S. P. 1538862; abst. Chem. Zentr. 1926, I, 2267.

5. L. Lilienfeld, Aust. P. 105040. E. P. 231804.

6. *Ibid.* Aust. P. 108107 Addn. to Aust. P. 104709. See Aust. P. 102305.

**Contributions of the Year 1928 in the Cellulose Ether Art.** H. Barthelemy<sup>1</sup> forms filaments by the extrusion of a cellulose ether or ester solution which is coagulated by the use of a liquid medium of such composition in respect to its rate of absorption of solvent from the filaments as to give the latter the desired properties. Among the materials which may be used are hydrocarbons (toluene, xylene, dimethylnaphthalene, decane, tridecane, hexadecane, terpenes, polyterpenes); cyclic hydrocarbons (cyclohexane, methylcyclohexane, tetrahydronaphthalene, decahydronaphthalene); alcohols (ethyl, propyl, butyl, glycol, glycerol, cyclohexanol, methylcyclohexanol, cyclohexylcarbinol, tetrahydro-*b*-naphthol); oleic and ricinoleic acids; ammonium, methyl, ethyl, propyl, butyl oleates, palmitates, stearates; halogenated compounds (di- and tri-chlorethylene, pentachlorethane, monochlorbenzene or -toluene, *a*-bromnaphthalene, 1.2.3-trichlorbenzene, benzyl chloride); nitrates ("benzonitrite, toluonitrite, xylonitrate"). They may also be coagulated by methyl or ethyl oleate or stearate<sup>2</sup>, or other emulsifying agents. To produce reduced luster in filaments from cellulose ethers<sup>3</sup> or from viscose<sup>4</sup> there is added before filament formation such substances as mono- and di-chlorbenzenes or -xylenes, or hydrogenated naphthalenes. If chlorbenzene is used<sup>5</sup>, the particles should be made progressively smaller as finer denier threads are spun in obtaining reduced luster effect. The delustering may be prevented or controlled by the addition to the bath of a small amount of sodium, potassium, ammonium or calcium

1. E. P. 282787; abst. C. A. 1928, **22**, 3989; J. S. C. I. 1929, **48**, 595-B; Silk Journal, 1928, **4**, #47, 70; Chem. Zentr. 1928, I, 1823. Compare U. S. P. 1107222.

2. E. P. 282790; abst. J. S. C. I. 1929, **48**, 714-B; Brit. Plastics, 1929, **1**, #5, 191; Chem. Zentr. 1928, I, 1824. F. P. 638899; abst. C. A. 1929, **23**, 514. See also E. P. 282788, 282791, 282793, 282794.

3. G. Bonwitt, E. P. 285863; abst. Chem. Zentr. 1929, I, 327.

4. E. P. 285066; abst. J. S. C. I. 1929, **48**, 203-B; Chem. Zentr. 1928, II, 2523; Kunst. 1929, **19**, 162.

5. E. P. 288222; abst. J. S. C. I. 1929, **48**, 353-B.

thiocyanate, or the ethylcellulose may be boiled in an aqueous thiocyanate solution<sup>1</sup>.

In the production of phosphorescent and luminous compositions<sup>2</sup>, such acquire greater permanence by grinding the salts generally used with plasticized cellulose ethers or esters.

In the preparation of thermoplastic materials containing cellulose ethers<sup>3</sup>, dibutyl phthalate is advocated as plasticizer, usually in combination with pigments as zinc oxide. For the manufacture of embossed knitted fabrics containing methyl- or ethyl-cellulose<sup>4</sup>, the fabric is first dampened with a softening agent such as a solution of acetone, methyl acetate, triacetin, *p*-toluenesulfonamide, diethyl phthalate, and finally embossed. Fabrics of cellulose ethers and esters may be dyed by means of a transfer<sup>5</sup>, the material being preferably moistened with a softener (as a 25% aqueous acetone) which is a solvent for the dye. Ribbons are made from wider fabrics by cutting the fabric into strips and sealing the severed edges against fraying or ravelling by fusing, dissolving or softening the edges, and then allowing them to solidify. In the case of the thermoplastic fabrics such as those made of methyl- or ethyl-cellulose<sup>6</sup>, the fabric is cut into strips by a heated knife adapted to fuse the severed edges, or<sup>7</sup> the edges may be treated with a softener without the application of heat.

1. British Celanese, Ltd., E. P. 282722; abst. C. A. 1928, **22**, 3988; J. S. C. I. 1929, **48**, 353-B; Silk J. 1928, **4**, #47, 70; Chem. Zentr. 1928, I, 1923. F. P. 644985.

2. J. Beavis, E. P. 299228; abst. J. S. C. I. 1929, **48**, 64-B; Chem. Zentr. 1929, I, 1052.

3. British Celanese, Ltd., E. P. 282723; abst. C. A. 1928, **22**, 3988; J. S. C. I. 1928, **47**, 853-B; Chem. Zentr. 1928, I, 1923. Can. P. 285231. Belg. P. 343438. F. P. 644935.

4. *Ibid.* E. P. 291445; abst. C. A. 1929, **23**, 1289; J. S. C. I. 1929, **48**, 848-B.

5. *Ibid.* E. P. 293022; abst. C. A. 1929, **23**, 1514; J. S. C. I. 1929, **48**, 811-B; Silk J. 1928, **5**, #52, 80; Chem. Zentr. 1928, II, 1944. F. P. 656466; abst. C. A. 1929, **23**, 4351.

6. *Ibid.* E. P. 293858; abst. Silk J. 1928, **5**, #54, 88; Chem. Zentr. 1928, II, 2087.

7. *Ibid.* E. P. 297712; abst. C. A. 1929, **23**, 2838; J. S. C. I. 1929, **48**, 242-B; Chem. Zentr. 1929, I, 818.

Delustered fabrics or threads containing formyl-, acetyl-, propionyl-, butyryl-, methyl- or ethyl-cellulose<sup>1</sup>, may have their luster restored by ironing or calendering them while damp. Mottled effects may be produced by dampening only portions of the materials. In the fire-proofing of textile materials made of or containing cellulose ethers<sup>2</sup>, the textile is steeped in an aqueous solution at 15-16° containing arsenic, stibinic or phosphoric acids, rinsed and dried. Aluminum acetate may also be added to the steeping liquor. Cellulose ether fabrics may be water-proofed by filling the interstices of the fabric with a rubber solution<sup>3</sup>, and afterwards embossing<sup>4</sup>.

In the formation of fusible and soluble resins suitable for use in varnishes in conjunction with the cellulose ethers<sup>5</sup>, the final stage of condensation is effected in the presence of a soluble dihydrogen phosphate (calcium, sodium or potassium dihydrogen). In the manufacture of varnishes<sup>6</sup>, methyl- or ethyl-cellulose are used either with synthetic resins or dammar, kauri, manilla, sandarac, copals or ester gums, with plasticizers. In the coloring of cellulose ethers<sup>7</sup>, the materials are printed or stencilled by the application of coloring pastes containing di- or trichlorethylene or ethylene dichloride in conjunction with a starchy body and an azo dye solution, colophony or calcium resinate being recommended as thickening agents in this connection.

1. British Celanese, Ltd., E. P. 295043; abst. C. A. 1929, **23**, 2046; J. S. C. I. 1930, **49**, 370-B; Silk J. 1928, **5**, #55, 76; Chem. Zentr. 1930, **49**, 370-B.

2. *Ibid.* E. P. 296344; abst. C. A. 1929, **23**, 2569; J. S. C. I. 1929, **48**, 281-B; Chem. Zentr. 1929, **I**, 169.

3. *Ibid.* E. P. 296450; abst. C. A. 1929, **23**, 2582; J. S. C. I. 1930, **49**, 370-B; Chem. Zentr. 1929, **I**, 169.

4. *Ibid.* E. P. 296451; abst. C. A. 1929, **23**, 2582; J. S. C. I. 1930, **49**, 370-B; Silk J. 1928, **5**, #55, 78; Chem. Zentr. 1929, **I**, 169.

5. *Ibid.* E. P. 296674; abst. C. A. 1929, **23**, 2585; J. S. C. I. 1930, **49**, 470-B.

6. *Ibid.* E. P. 296675; abst. C. A. 1929, **23**, 2585; J. S. C. I. 1930, **49**, 338-B; Chem. Zentr. 1929, **I**, 451; Kunst. 1929, **19**, 162.

7. *Ibid.* E. P. 297848; abst. C. A. 1929, **23**, 2836; J. S. C. I. 1930, **49**, 237-B; Chem. Zentr. 1929, **I**, 1153. See also E. P. 284376; abst. C. A. 1928, **22**, 4834.

In the coating of smooth surfaces of or containing methyl-, ethyl- or benzyl-cellulose<sup>1</sup>, an intermediate nitro-cellulose lacquer is used to aid adhesion, or<sup>2</sup>, the cellulose ether may constitute the base or first coat, followed by the application of a solution of cellulose acetate. It has been found<sup>3</sup>, that fabrics consisting of or containing methyl-, ethyl- or benzyl-cellulose if treated with an aluminum salt (basic acetate), may be ironed at a higher temperature without the iron sticking to them. Acetic acid and ammonium sulfocyanide may be used in conjunction with the aluminum, the treatment also rendering the fabrics waterproof.

Varnishes and lacquers for coating metallic and other surfaces<sup>4</sup> comprise a cellulose ether or ester and a synthetic ketone-phenol-aldehyde resin<sup>5</sup>, with gums and high-boiling plasticizers. To facilitate obtainment of sharply defined outlines on cellulose ether or ester fabrics<sup>6</sup>, the materials are treated before application of dyes, with basic aluminum acetate to which is added formic or acetic acids. In the production of laminated products<sup>7</sup>, cellulose ethers preferably of a fibrous character are mixed with vegetable, animal or mineral fibers in a beating engine, and the resulting stock run on a paper or board machine. The sheets thus obtained are subjected to heat and pressure, the products obtained finding use in the arts as electric insulators or in the manufacture of wheels and gears.

1. British Celanese, Ltd., E. P. 298608; abst. C. A. 1929, **23**, 3098; J. S. C. I. 1930, **49**, 431-B; Brit. Plastics, 1930, **2**, #13, 52.

2. *Ibid.* E. P. 298616; abst. C. A. 1929, **23**, 3115; J. S. C. I. 1930, **49**, 337-B; Chem. Zentr. 1929, I, 1067.

3. *Ibid.* E. P. 299058; abst. C. A. 1929, **23**, 3111; J. S. C. I. 1929, **48**, 716-B; Silk J. 1929, **5**, #57, 72; Chem. Zentr. 1929, I, 1168.

4. *Ibid.* E. P. 299781; abst. C. A. 1929, **23**, 3588; J. S. C. I. 1930, **49**, 571-B; Chem. Zentr. 1929, I, 1275; Kunst. 1929, **19**, 259.

5. *Ibid.* Of the type described in E. P. 299065; abst. C. A. 1929, **23**, 3115; J. S. C. I. 1930, **49**, 338-B.

6. *Ibid.* E. P. 299849; abst. C. A. 1929, **23**, 3584; J. S. C. I. 1930, **49**, 237-B; Chem. Zentr. 1929, I, 1514.

7. *Ibid.* E. P. 301428; abst. C. A. 1929, **23**, 4072; J. S. C. I. 1930, **49**, 369-B; Chem. Zentr. 1929, I, 2493.

In coating compositions containing cellulose ether<sup>1</sup>, naphthalene may be used as a softener with a volatile solvent to which natural or synthetic resins may be added as modifying components. In the loading of yarns or threads of methyl-, ethyl- or benzyl-cellulose<sup>2</sup>, a soluble salt of tin, zinc, aluminum, bismuth or tungsten is employed in conjunction with a following bath of tannin, soluble phosphate or silicate. In addition to the loading, the goods show less tendency to slip, ladder or split, and exhibit greater fullness and volume.

Colored cellulose ether films are obtained by applying thereto various dissolved or solubilized azo colors, especially valuable in photography. Insoluble pigments may be added to induce opacity<sup>3</sup>. In the loading, mordanting and dyeing of materials made of or containing ethyl- or benzyl-cellulose<sup>4</sup>, the material is treated with alkaline tin solutions (sodium stannate) and sodium sulfocyanide under conditions which bring about a partial regeneration of the cellulose. Material so treated may be dyed with direct, mordant, or vat dyes, or the usual basic colors. In another method of dyeing cellulose ethers or esters<sup>5</sup>, a suitable arylamine (*p*-aminodiphenylamine) is oxidized on the fiber with *p*-toluenesulfonchloramide or its sodium salt in presence of an acid or a catalyst (vanadium chloride). Or<sup>6</sup>, a dyeing, printing or stencilling effect may be produced by introduc-

1. British Celanese, Ltd., E. P. 301497; abst. C. A. 1929, **23**, 4071; Chem. Zentr. 1929, I, 1751.

2. British Celanese Ltd., H. Dreyfus and G. Ellis, E. P. 285941; abst. C. A. 1929, **23**, 290; J. S. C. I. 1928, **47**, 330-B; Silk J. 1928, **5**, #49, 78; Chem. Zentr. 1928, II, 204. Can. P. 276516. Belg. P. 344890.

3. British Celanese Ltd., and G. Ellis, E. P. 285431; abst. C. A. 1928, **22**, 4834; Chem. Zentr. 1928, I, 3132. F. P. 648137; abst. C. A. 1929, **23**, 2822. See also E. P. 224681, 227183, 237943, 239470, 253978, 263260.

4. British Celanese Ltd., and G. Ellis, E. P. 302775; abst. C. A. 1929, **23**, 4353; J. S. C. I. 1929, **48**, 169-B; Silk J. 1929, **5**, #59, 72; Chem. Zentr. 1929, I, 2718.

5. British Celanese Ltd., G. Ellis and H. Olpin, E. P. 298699; abst. C. A. 1929, **23**, 3110; J. S. C. I. 1928, **47**, 926-B; Chem. Zentr. 1929, I, 1153. See also E. P. 273820.

6. British Celanese Ltd., G. Ellis and H. Olpin, E. P. 299349; abst. C. A. 1929, **23**, 3355; J. S. C. I. 1929, **48**, 15-B.

ing at least one *b*-ketoacyl group into dyes containing amino groups, which may be of the azo, nitrodiarylamine, nitrodiaryl, nitrodiarylmethane or anthraquinone series and usually unsulfonated. Examples are the acetoacetyl derivatives of aminoazobenzene (greenish-yellow), 2,4-dinitro-4'-aminodiphenylamine (golden-yellow) and 1,4-diamino-2-methylantraquinone (orange).

Dyeing may also be effected by coupling on the material<sup>1</sup> either (1) diazotized amino-*b*-ketoacidylamino) or amino-*b*-ketoacidylamino)-azo compounds with suitable components, or (2) diazotized amines or aminoazo compounds with acetoacetic arylides. Black dyeings are obtained<sup>2</sup> by means of one or more unsulfonated azo dye-stuffs obtained from aminophenols or their nuclear substitution products and containing the azo group linked to the naphthalene nucleus in a position ortho or peri to an auxochromic group. Specific dyes giving red shades on cellulose ethers and esters result when monoazo or disazo dyes from naphthylenediamines or their nuclear substitution products are used<sup>3</sup>. The British Celanese, Ltd.<sup>4</sup>, have described a process and apparatus for cellulose ether or ester filament formation by the dry-spinning method, by extruding the spinning solution into closed chambers, the full evaporative capacity of the air being utilized by employing collector devices adapted to limit the passage for the air so that practically the whole is constrained to pass through the immediate vicinity of the nozzle.

1. British Celanese Ltd., G. Ellis and H. Olpin, E. P. 300929; abst. C. A. 1929, **23**, 4083; J. S. C. I. 1929, **48**, 127-B; Chem. Zentr. 1929, I, 1619.

2. British Celanese Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 298993; abst. C. A. 1929, **23**, 3110; J. S. C. I. 1929, **48**, 51-B; Chem. Zentr. 1929, I, 1154. Cf. E. P. 219349, 224925, 242393, 242711, 269960, 273819, 273820.

3. *Ibid.* E. P. 299343; abst. C. A. 1929, **23**, 3355; J. S. C. I. 1929, **48**, 15-B; Chem. Zentr. 1929, I, 1154.

4. British Celanese Ltd., E. Kinsella, J. Bower and W. Taylor, E. P. 300998; abst. C. A. 1929, **23**, 4072; J. S. C. I. 1929, **48**, 203-B; Chem. Zentr. 1929, I, 1635. See E. P. 203092. F. P. 566385; abst. Chem. Zentr. 1924, I, 2760; Faserstoffe, 1924, **6**, 67.



Cellulose ethers may be dyed with sulfuric esters of anthraquinonylamino alcohols or their alkali salts, wherein one or both of the hydrogen atoms are replaced by one or two aliphatic groupings containing one or more hydroxy groups. For instance, sodium 1-*b*-oxyethylaminoanthraquinone sulfate dyes scarlet<sup>1</sup>. Dry dispersed dye preparations suitable for dyeing cellulose ethers may be made with the aid of a product obtained by heating ligninsulfonic acid with alkali metal hydroxides or carbonates<sup>2</sup>.

H. Buel<sup>3</sup> waterproofs pulp milk bottles, egg or food wrappers with ethylcellulose acetate (ethylacetylcellulose) in which formaldehyde is added to "harden" the film. A cellulose ether composition has been described by S. Carroll<sup>4</sup> in which water-insoluble ethylcellulose is dissolved in mono-, di- or tri-acetin in conjunction with a volatile solvent (a mixture of methyl alcohol and methyl acetate). W. Charch and K. Prindle<sup>5</sup> waterproof hydrated cellulose (cellophane, flexoloid, biophane, dramatine, brilliantine, smaline, cello-glass, glassolyn) by treating both sides in film form with a cellulose ester or ether, preferably aided by ester gum or dammar and a high-boiler as dibutyl phthalate.

C. Claessen<sup>6</sup> has analyzed the Lilienfeld cellulose ether silk patents, while there have been described mixed cellulose esters containing the acetic radical with stearic, palmitic, lauric, myristic, heptylic, isovaleric, *n*-valeric, cyclohexanecarboxylic, crotonic, cinnamic, hydrocinnamic,

1. British Celanese Ltd., and C. Olpin, E. P. 285641; abst. C. A. 1929, **23**, 288; J. S. C. I. 1928, **47**, 364-B; Chem. Zentr. 1928, I, 3116.

2. British Celanese Ltd., H. Adams and A. Shepherdson, E. P. 301549; abst. C. A. 1929, **23**, 4079; J. S. C. I. 1929, **48**, 124-B; Chem. Zentr. 1929, I, 2829.

3. U. S. P. 1680934; abst. C. A. 1928, **22**, 3712; J. S. C. I. 1928, **47**, 782-B; Chem. Zentr. 1928, II, 2083.

4. U. S. P. 1658369; abst. C. A. 1928, **22**, 1237; *Plastics*, 1928, 262; J. S. C. I. 1927, **46**, 295-B; Chem. Zentr. 1928, I, 1923; *Kunst.* 1929, **19**, 161.

5. U. S. P. 1737187; abst. J. S. C. I. 1930, **49**, 53-B. E. P. 283109; abst. J. S. C. I. 1929, **48**, 715-B; *Br. Plastics*, 1929, **1**, 191; Chem. Zentr. 1928, I, 1923.

6. Rayon J. 1928, **3**, No. 4, 24, 39; abst. C. A. 1929, **23**, 520.

undecyclenic, *o*-methoxybenzoic and benzoic acids. Instead of cotton, the cellulose ethers may be used, as an example, methylcellulose giving with stearic acid a methylcellulose stearate. Cellulose acetopropionate and butyro-*o*-methoxybenzoate<sup>1</sup> have also been described. These may be combined with the cellulose ethers to produce ethercellulose esters. Aceto-valerates, -caproates, -caprates and -pelargonates<sup>2</sup> have also been granted patent protection, alone and in combination with the cellulose ethers.

Societe Clement & Riviere<sup>3</sup> reduce the viscosity of benzylcellulose in solution by the addition thereto of such basic agents as sodium or ammonium hydroxides, or ammonia in the gaseous form. In producing artificial cellulose ether and ester filaments, Courtaulds, Ltd.<sup>4</sup>, maintain the solution at the spinning nozzle and the air in the spinning chamber which is in the neighborhood of the nozzle, at practically the same temperature.

J. Davidson<sup>5</sup> produces thermoplastic masses of ethylcellulose with polyglycols as diethylene-, triethylene-, and ethylenepropylene-glycol. In producing differential colored fabrics containing cellulose ethers or esters, C. Dreyfus and H. Platt<sup>6</sup> produce differential colored fabrics by imprinting a design of cellulose ether in the dissolved state, a fabric of a cellulose ester as cellulose acetate is used as the base upon which the design is printed. C. Dreyfus has described the preparation of methyl-, ethyl-, and benzyl-cellulose in which ortho- or meta-phosphoric acid is used as catalyst. Cloth

1. H. Clarke and C. Malm, E. P. 290571; Addn. to E. P. 287880; abst. J. S. C. I. 1930, **49**, 279-B; Br. Plastics, 1930, **1**, 498; Chem. Zentr. 1928, II, 1282.

2. H. Clarke, C. Malm and R. Stinchfield, E. P. 287880; abst. C. A. 1929, **23**, 512; J. S. C. I. 1930, **49**, 279-B; Chem. Zentr. 1928, II, 304.

3. F. P. 675086; abst. C. A. 1930, **24**, 2882.

4. Can. P. 282326; abst. C. A. 1928, **22**, 3529.

5. U. S. P. 1693746; abst. J. S. C. I. 1929, **48**, 554; Chem. Zentr. 1929, I, 1517.

6. U. S. P. 1689426; abst. C. A. 1929, **23**, 289; J. S. C. I. 1929, **48**, 514-B; Chem. Zentr. 1929, I, 1619. E. P. 295582; abst. C. A. 1929, **23**, 2305; J. S. C. I. 1930, **49**, 54-B; Silk. J. 1928, **5**, #55, 76; Chem. Zentr. 1928, II, 2754.

is coated with acetyl-, butyryl- or ethyl-cellulose<sup>1</sup> by spreading the ether on a polished surface and drying, the cloth wetted with an appropriate solvent being spread upon another polished surface and the two surfaces brought together with pressure and heat.

In the manufacture of coated objects<sup>2</sup>, films or cloth having a surface of cellulose acetate are coated with a cellulose ether in a solvent which is not a solvent of the cellulose acetate (e.g. benzene), pressure being applied. A metallic effect is obtained by rubbing the surface with bismuth or antimony oxychlorides and covering with a transparent layer of cellulose ether or ester.

In the dyeing or printing of materials composed of or containing the cellulose ethers, H. Dreyfus<sup>3</sup> first swells the ether with formic, acetic, glycollic or lactic acid, then colors with an aqueous dispersion of an insoluble colored compound which has previously been treated with a dispersing agent (sulfuric acid) followed by diazotization and development on the fiber. As swelling agents for water-insoluble cellulose ethers<sup>4</sup>, are potassium, sodium and ammonium isothiocyanates, cyanates, and isocyanates; urea, urethanes, thiourea, thiourethanes, guanidine and diethyldiphenylurea. As a valuable plasticizing agent for ethyl- or benzyl-cellulose<sup>5</sup>, chloretone (trichlorotertiarybutyl alcohol, chlorbutol) has been brought forward. Cellulose ethers may be colored with tinctorial substances of the azo, diarylamine, nitrodiarylmethane or anthrapyridone series containing one or more urethane residues, yellow shades being

1. F. P. 634345; abst. C. A. 1928, **22**, 3788; Chem. Zentr. 1928, I, 3132; Kunst. 1929, **19**, 139.

2. C. Dreyfus, F. P. 637113; abst. C. A. 1929, **23**, 704; Plastics, 1929, **5**, 638. E. P. 274841; abst. C. A. 1928, **22**, 2273; J. S. C. I. 1928, **47**, 782-B; Chem. Zentr. 1927, II, 2788. Ital. P. 259388.

3. E. P. 285942; abst. C. A. 1929, **23**, 288; J. S. C. I. 1928, **47**, 331-B; Chem. Zentr. 1928, I, 3117. Compare E. P. 284376. F. P. 642473; abst. C. A. 1929, **23**, 1286. F. P. 643323.

4. E. P. 284798; abst. C. A. 1928, **22**, 4836; J. S. C. I. 1928, **47**, 444; Chem. Zentr. 1928, I, 2889. F. P. 634165, and Addn. 34391.

5. U. S. P. 1661169; abst. C. A. 1928, **22**, 1473; J. S. C. I. 1928, **47**, 295-B; Plastics. 1928, **4**, 688; Kunst. 1929, **19**, 162. E. P. 205195; abst. C. A. 1924, **18**, 1199; J. S. C. I. 1923, **42**, 1172-A; Kunst. 1924, **14**, 91; Chem. Zentr. 1924, I, 716.

produced<sup>1</sup>, or azo compounds containing one or more *w*-groups in the diazo component<sup>2</sup> may be used.

In the coloring of cellulose ethers or esters<sup>3</sup>, compounds are applied in which an aryl dye nucleus is linked to one or more thiourethane residues. The dyes may be prepared by heating the corresponding isothiocyanate compounds with alcohols or alcoholic caustic alkali, or by treating the corresponding thiourea chloride compounds with alcoholates. Cellulose ether compounds may be mordanted with solutions of mordant metal salts (other than ferric salts) and then dyed with mordant dyes. If temperatures above 80° are used, a protective agent is added to prevent delustering. Examples are alizarin on an aluminum sulfacetate or nitrate-acetate mordant, and Modern Heliotrope DH on a lactate, citrate or glycollate (as chromium, aluminum or sodium) base<sup>4</sup>. Or<sup>5</sup>, compounds of hydroxylated alkyl ethers or thioethers obtained from colored phenols or thiophenols (other than azo compounds) by the action of suitable chlorhydrins, alkylene oxides or acetone may be used. Examples are: 1-*b*-hydroxyethylthiolanthraquinone (yellow), 1-By-dihydroxypropylthiolanthraquinone (yellow), 1-methylamino-4-By-dihydroxypropylthiolanthraquinone (reddish-orange), 1-acetamido-4-B-hydroxyethoxyanthraquinone (golden-yellow), or 1-By-dihydroxypropylthiolanthrapyridone (from chloranthrapyridone and By-dihydroxypropyl mercaptan; yellow).

1. U. S. P. 1735960; abst. C. A. 1930, **24**, 972; J. S. C. I. 1930, **49**, 54-B. E. P. 292452; abst. C. A. 1929, **23**, 1513; Silk. J. 1928, **5**, #52, 80; Chem. Zentr. 1928, II, 1944.

2. E. P. 292453; abst. C. A. 1929, **23**, 1513; Silk. J. 1928, **5**, #52, 80; Chem. Zentr. 1928, II, 1944. Can. P. 281190.

3. U. S. P. 1735963; abst. J. S. C. I. 1930, **49**, 54-B. E. P. 291816; abst. C. A. 1929, **23**, 1287; J. S. C. I. 1928, **47**, 639-B. F. P. addn. 32948 to F. P. 627072; abst. C. A. 1929, **23**, 1287; Chem. Zentr. 1928, II, 392. Can. P. 285799. Patent cites E. P. 291118, 285968, 285969.

4. U. S. P. 1779464; abst. C. A. 1931, **25**, 217; J. S. C. I. 1930, **49**, 1148-B. E. P. 287204; abst. C. A. 1929, **23**, 528; J. S. C. I. 1928, **47**, 402-B; Chem. Zentr. 1928, II, 292. F. P. 644937.

5. U. S. P. 1783607; abst. C. A. 1931, **25**, 421; J. S. C. I. 1931, **50**, 155-B. E. P. 285969; abst. C. A. 1929, **23**, 288; J. S. C. I. 1928, **47**, 331-B; Chem. Zentr. 1928, I, 3116.

Dyed effects on methyl-, ethyl- or benzyl-cellulose are producable by employing azo compounds containing one or more amino groups substituted by one or more aliphatic side chains, each containing two or more hydroxyl groups but no carboxyl group<sup>1</sup>. The dyestuffs are usually sufficiently soluble to be applied in aqueous solution, but may be pre-treated with solubilizing agents<sup>2</sup>. In combined dyeing and mordanting cellulose ether threads or fabrics<sup>3</sup>, preliminary treatment with swelling agents is followed by mordanting with iron chloride or nitrate, chromium chloride or acetate, aluminum acetate or sulfate, or stannous chloride.

Cellulose ether and ester fabrics are rendered less liable to develop faults due to lack of cohesion, by a single or multiple impregnation at 80-100° with aqueous dispersions containing at least 10% of oleic, stearic, palmitic, sulfo-phenylstearic, sulfohydroxyphenylstearic or sulfonaphthylstearic acids or resin soaps. Paraffin, naphthene or terpene hydrocarbons are also applicable. Cellulose ethers may likewise be dyed with compounds in which an aryl dye nucleus is connected to an amino group or aliphatically

1. U. S. P. 1735961; abst. C. A. 1930, **24**, 972; J. S. C. I. 1930, **49**, 54-B. E. P. 292180; abst. C. A. 1929, **23**, 1513; J. S. C. I. 1928, **47**, 639-B; Silk J. 1928, **5**, #52, 80; Chem. Zentr. 1928, II, 1943.

2. British Celanese Ltd., and G. Ellis, E. P. 219349; abst. C. A. 1925, **19**, 579; J. S. C. I. 1924, **43**, 906-B; Ann. Rep. S. C. I. 1924, **9**, 138, 166; Chem. Zentr. 1924, II, 2703. E. P. 224925; abst. C. A. 1925, **19**, 1952; J. S. C. I. 1925, **44**, 39-B; Ann. Rep. S. C. I. 1925, **10**, 136; Chem. Zentr. 1925, I, 1653. F. P. 568655; abst. Chem. Zentr. 1927, I, 3139. E. P. 242393; abst. C. A. 1926, **20**, 3822; J. S. C. I. 1926, **45**, 87-B; Ann. Rep. S. C. I. 1926, **11**, 153; Chem. Zentr. 1926, I, 2971. British Celanese Ltd., G. Ellis and W. Goldthorpe, E. P. 242711; abst. C. A. 1926, **20**, 3822; J. S. C. I. 1926, **45**, 50-B; Ann. Rep. S. C. I. 1926, **11**, 154; Chem. Zentr. 1926, I, 2970. E. P. 269960; abst. C. A. 1928, **22**, 1482; J. S. C. I. 1927, **46**, 475-B; Chem. Zentr. 1927, II, 1205. British Celanese, Ltd., and G. Ellis, E. P. 273819; abst. C. A. 1928, **22**, 2066; J. S. C. I. 1927, **46**, 650-B; Chem. Zentr. 1927, II, 2574. E. P. 273820; abst. C. A. 1928, **22**, 2066; J. S. C. I. 1927, **46**, 650-B; Chem. Zentr. 1927, II, 2715. F. P. 568655, and Addn. 33247. Can. P. 276515. Ital. P. 222812. Belg. P. 340536.

3. E. P. 285948; abst. C. A. 1929, **23**, 288; J. S. C. I. 1928, **47**, 331-B; Chem. Zentr. 1928, I, 3116. Can. P. 285801; abst. C. A. 1929, **23**, 1267.

substituted amino group<sup>1</sup>. In an analogous method<sup>2</sup>, the dyestuff comprises an aryl group linked to one or more thiocyanate, cyanate, isothiocyanate or simple substituted urea or thiourea residues.

Cellulose ether filaments or fabrics may be mordanted with at least a 15% concentration of aluminum sulfate, alums, chromium chloride, fluoride or bisulfite, assisting substances being potassium bitartrate or oxalic acid<sup>3</sup>. In dyeing scarlet shades<sup>4</sup>, 1-(*b*-hydroxyethyl)-aminoanthraquinone, solubilized with Turkey red oil has been patented, as also has anthraquinone-1-*b*-hydroxyethylmercaptan obtained from anthraquinone-1-mercaptan and ethylene chlorhydrin. Ethylcellulose threads, yarns and films may be dyed<sup>5</sup> by stated coloring matters which heretofore were applicable only to the cellulose esters, detailed lists being given.

Aliphatic esters of maleic and fumaric acids<sup>6</sup> (dimethyl, diethyl, di-isobutyl) are obtained with ethylcellulose in the fabrication of plastic compounds and celluloid substitutes. J. Duclaux reinforces glass<sup>7</sup> by placing a film of methyl- or ethyl-cellulose between two sheets of glass, and if it is desired to cut out light waves lengths of less than 0.00033 mm. there is incorporated in the film such substances as lead, mercury or bismuth stannates, molyb-

1. E. P. 292181; abst. C. A. 1929, **23**, 1514; J. S. C. I. 1928, **47**, 639-B; Silk J. 1928, **5**, #52, 80; Chem. Zentr. 1928, II, 1943.

2. E. P. 291118; abst. C. A. 1929, **23**, 1287; J. S. C. I. 1928, **47**, 601-B; Chem. Zentr. 1928, II, 1943. F. P. 627072; abst. Chem. Zentr. 1928, I, 2007.

3. E. P. 286761; abst. C. A. 1929, **23**, 528; J. S. C. I. 1928, **47**, 402-B; Chem. Zentr. 1928, II, 1267. F. P. 644936.

4. E. P. 285968; abst. C. A. 1929, **23**, 288; J. S. C. I. 1928, **47**, 331-B. F. P. 627071; abst. Chem. Zentr. 1928, I, 2006. Addn. 32949 and 35560, to F. P. 627071.

5. E. P. 285104; abst. C. A. 1928, **22**, 4834; J. S. C. I. 1928, **47**, 364-B; Chem. Zentr. 1928, I, 2874. Patent cites E. P. 196952, 196953, 196954, 197281.

6. O. Drossbach and O. Jordan, U. S. P. 1677753; abst. C. A. 1928, **22**, 3300; J. S. C. I. 1929, **48**, 13-B; Chem. Zentr. 1928, II, 2690. D. R. P. 512321; abst. Chim. et Ind. 1931, **25**, 1218.

7. F. P. 648990; abst. C. A. 1929, **23**, 2798. Belg. P. 300944. Patent cites F. P. 418257, 439644, 467303; abst. Rev. Chim. Ind. 1914, **25**, 260.

dates or tungstates, stilbine, dibenzyl or propyl, butyl or amyl alcohols. In coating metal surfaces<sup>1</sup>, a primary coat of glycerol and phthalic acid is applied, followed by a top coat of ethylcellulose, or by various described, difficultly definable mixed fatty acid esters.

A. Eichengruen<sup>2</sup> produces pressed masses, by extruding highly concentrated, viscous solutions of cellulose ethers, with or without softening agents in the form of a heated paste through narrow apertures. The extruded material on reduction of pressure, swells to a porous mass which may be pressed to form in heated molds. In working up cellulose derivatives<sup>3</sup>, cellulose ether is treated in the cold with a non-solvent, and after removal of excess of liquid, the swollen material is converted into a homogeneous mass with a plasticizer, and afterwards worked up into the desired form. Yellow dyeings on cellulose ethers and esters in fast, non-phototropic shades are obtained with azo dyes prepared by condensing 4-aminoazobenzene with 1-chlor-2,6-dinitrobenzenesulfonic acid or with 1-chlor-4-nitrobenzene-2-sulfonic acid.

C. Fox and L. Hall<sup>4</sup> have pointed out the intrinsic properties of the cellulose ethers, while K. Freudenberg alone<sup>5</sup>, and in conjunction with E. Braun<sup>6</sup> has studied the methylcelluloses, and found that cellulose may be methylated by employing a large excess of methyl sulfate and concentrated potash at 20° to a fibrous trimethyl derivative (44-45% methoxyl) which yields viscous solutions in chloroform, tetrachlorethane and acetic acid. This methylcellu-

1. E. I. Du Pont de Nemours & Co., E. P. 287940; abst. J. S. C. I. 1929, **48**, 989-B; Chem. Zentr. 1928, II, 2072.

2. E. P. 290989; abst. C. A. 1929, **23**, 1267; J. S. C. I. 1929, **48**, 893-B; Brit. Plastics. 1929, **1**, #7, 284; Plastics, 1929, **5**, 390. Compare E. P. 147904, 171432.

3. E. P. 291386; abst. J. S. C. I. 1930, **49**, 138-B; Brit. Plastics, 1930, **1**, #10, 447.

4. Die Kunstseide. 1928, #1, 10; J. S. C. I. 1927, **46**, 281-T.

5. Ann. Chem. 1928, **461**, #2, 130; abst. J. S. C. I. 1928, **47**, 743-A; C. A. 1928, **22**, 3292.

6. Ann. Chem. 1928, **460**, 288; abst. J. S. C. I. 1928, **47**, 399-A; C. A. 1928, **22**, 3635; Chem. Zentr. 1928, I, 1848.

lose is rapidly dissolved by ethereal hydrogen chloride at 30°, yielding 2.3.6-trimethyl-1-chloroglucose which on treatment with sodium in ether gives trimethylglucose anhydride. This is considered to dispose of the view of Hess, that trimethylcellulose is a monomolecular trimethylglucose anhydride. Upon further investigations<sup>1</sup>, purified lignin when methylated, was found to yield considerable methylcellulose to chloroform or acetic acid.

H. Gardner<sup>2</sup> finds the character of cellulose ether and other artificial cellulose filament products are considerably improved in appearance by treatment with a soluble titanium salt, as sulfate or titanium potassium oxalate in that it acquires a pleasing semi-delusterized appearance. In conjunction with C. Knauss<sup>3</sup>, tests have been made and recorded of the relative light permanency of cellulose ether dissolved in benzene and toluene with the following plasticizers added thereto: ethyl acetylglcolate, ethyl *m*-toluenesulfonamide, diethyl, dibutyl and diamyl phthalates, ethyl-toluenesulfonamide, hexol, *p*-toluenesulfonanilid, tricresyl phosphate, *o*-chloracetanilid, *o*-acetanisidine, each with 1% (on the weight of the lacquer) of dicyandiamine or urea added. Best results were obtained with tricresyl phosphate.

In a study of the cellulose sulfates<sup>4</sup>, attempts have been made to decide whether the sulfate is actually a cellulose derivative, by means of the use of hydrogen chloride in methyl alcohol, thereby partially etherifying the cellulose<sup>5</sup>.

1. K. Freudenberg, M. Harder and L. Markert in part with E. Spiess, Ber. 1928, **61B**, 1760; abst. C. A. 1929, **23**, 276; J. S. C. I. 1928, **47**, 1227-A; Chem. Zentr. 1928, II, 2550.

2. U. S. P. 1692372; abst. C. A. 1929, **23**, 719; J. S. C. I. 1929, **48**, 169-B. E. P. 290263; abst. J. S. C. I. 1929, **48**, 430-B; Chem. Zentr. 1928, II, 1407. D. R. P. 531079. F. P. 647013.

3. Am. Paint & Varnish Manufs. Assoc. Circ. 1928, No. 338, 657; abst. C. A. 1929, **23**, 276; J. S. C. I. 1928, **47**, 888-B.

4. E. Gebauer-Fulnegg, W. Stevens and O. Dingler, Ber. 1928, **61B**, 2000; abst. C. A. 1930, **24**, 1502; J. S. C. I. 1928, **47**, 1226-A; Chem. Zentr. 1929, I, 47; J. A. C. S. 1930, **52**, 2849.

5. W. Glover and C. Diamond, Can. P. 277024; abst. C. A. 1928, **22**, 2663.



Sustaining protests of W. Grotte<sup>1</sup> of Cleveland, Ohio, the U. S. Customs Court has handed down a decision that imported insulating material composed of cellulose ether, dye, China clay and barytes is not a compound of "a cellulose esters or ethers" and is dutiable at 25% *ad valorem* by Paragraph 31, Tariff Act of 1922.

J. Guerard<sup>2</sup> has evolved a process for preparing printing blocks and varnishes for printing plates, in which cellulose ether in acetone to which dissolved resins are added, forms the coating for the support. Sheet materials for use as supports for photographic emulsions and images are formed of cellulose ethers, mixed with finely divided cellulose and a white opaque pigment (zinc or titanium oxides)<sup>3</sup>. A plasticizer and small amount of cedar wood oil is incorporated with the carbohydrate ether.

Diphenylmonocresyl phosphate and phenyldicresyl phosphate have been brought forward as cellulose ether and ester plasticizer and flexilizing agents<sup>4</sup>, the relative proportions of the two compounds being so adjusted that the final mixture corresponds in composition to a mixture of 55% triphenyl phosphate and 45% tricresyl phosphate. Either this is an attempt at patent circumlocution, or the contention of the patentees is correct that in this way the reduction in inflammability imparted by triphenyl phosphate and pliability imparted by tricresyl phosphate is sustained.

Stable and permanent derivatives are produced<sup>5</sup> by oxidizing a cellulose or starch compound containing a CSS

1. *Plastics*, 1928, **4**, 592.

2. E. P. 294987; abst. C. A. 1929, **23**, 2050.

3. H. Hands and Spicers, Ltd., E. P. 282980; abst. J. S. C. I. 1928, **47**, 213-B; *Chem. Zentr.* 1928, I, 1824; *Kunst.* 1929, **19**, 138. D. R. P. 468743; abst. C. A. 1929, **23**, 781; *Chem. Zentr.* 1929, I, 340. F. P. 625165.

4. H. Hands, and Spicers, Ltd., E. P. 294008; abst. C. A. 1929, **23**, 1749; J. S. C. I. 1928, **47**, 810-B; *Chem. Zentr.* 1928, II, 2087. F. P. 659141; abst. C. A. 1929, **23**, 5283. Australia P. 15154. See India P. 12998, 13089, 13856. Ital. P. 264194, 271718, 272478. D. R. P. 527737. F. P. 659141. Aust. P. 118246; abst. *Kunst.* 1931, **21**, 19.

5. W. Harrison, E. P. 286332; abst. C. A. 1929, **23**, 155; *Chem. Zentr.* 1928, II, 305. U. S. P. 1684732; abst. C. A. 1928, **22**, 4536. D. R. P. 497240; abst. C. A. 1930, **24**, 3646.

group, in the presence of ammonia or an ammonium derivative not containing organic constituents such as hydroxylamine. Oxidizing agents capable of oxidizing hydrogen bisulfide may be used, as ferricyanides, bichromates, peroxides, nitrous acid, sulfur dioxide, ferric salts and air, or oxygen with or without oxygen carriers. Oxygen may be used in the nascent state as generated by electrolysis. As starting materials, cellulose or starch xanthates and cellulose dixanthate may be used. In an analogous process<sup>1</sup>, ammonia is employed in which at least one atom of hydrogen is reactive, and in which one or both of the other hydrogen atoms may be replaced by an alkyl, aryl or aralkyl group (acetamide, benzamide, phthalimide, cyanamide, dicyanodiamide, dicyanimide, guanidine) or thiourea or its derivatives. Products are obtained suitable for film and filament formation.

Yellow to orange shades may be dyed on cellulose ether and ester filaments and fabrics<sup>2</sup>, with azo dyes containing not more than one sulfonic or carboxyl group, made by coupling a diazotized arylamine with fused-ring derivatives of 5-membered ring compounds capable of coupling. Examples are: sulfanilic acid or 2,5-dichloraniline with 2-methylin-dole (yellow); aniline-*o*-sulfonic acid with 3-hydroxythionaphthene (S-oxide of thioindoxyl; orange); and 6-chlor-*o*-toluidine with oxindole-6-sulfonic acid (greenish yellow).

K. Hess and A. Mueller<sup>3</sup> have prepared triethylcellulose in 70% yield by repeated treatment of purified cotton with ethyl sulfate and sodium hydroxide, and found the same properties as triethylcellulose prepared from other sources.

1. E. P. 286331; abst. C. A. 1929, **23**, 155; Chem. Zentr. 1928, II, 305.

2. W. Hentrich, R. Knoche and M. Hardtmann, U. S. P. 1711890; abst. C. A. 1929, **23**, 3355; J. S. C. I. 1929, **48**, 515-B; Chem. Zentr. 1929, II, 1748. E. P. 284652; abst. C. A. 1928, **22**, 4834; J. S. C. I. 1929, **48**, 678-B; Chem. Zentr. 1928, I, 2997. E. P. 301564; abst. C. A. 1929, **23**, 4350; J. S. C. I. 1929, **48**, 127-B. F. P. 640746; abst. Chem. Zentr. 1928, II, 2064. D. R. P. 480904; abst. C. A. 1929, **23**, 5048; Chem. Zentr. 1929, II, 2375.

3. Ann. Chem. 1828, **466**, 94; abst. C. A. 1929, **23**, 1118; J. S. C. I. 1928, **47**, 1360-A; Chem. Zentr. 1929, I, 235.

The ether crystallized best from a 0.2-0.5% solution in alcohol-benzene. Hydrolysis by HCl in ethyl alcohol gave triethylethylglucoside; further hydrolysis, triethylglucose. K. Hess and C. Trogus<sup>1</sup> in conducting an X-ray investigation on cellulose and its ethers, have reproduced X-ray diagrams of hexa-acetylbiosans, cellulose hydrate, hexamethylbiosan, trimethylcellulose and ByC-trimethylcellulose. K. Hess<sup>2</sup> finds no real discrepancy between the results of methylation of cellulose by K. Hess and H. Pichlmayr<sup>3</sup>, by H. Urban<sup>4</sup>, and by K. Freudenberg and E. Braun<sup>5</sup>. A sample of the latter was partly soluble in water with agitation, or after swelling and dissolving in indifferent solvents. The water-soluble fractions in each case had the same rotatory power and X-ray diagrams. Such differences as appear to exist are accountable by preservation of the non-cellulosic coating of the fiber due to incomplete purification in the case of "cotton," from which "insoluble" trimethylcellulose is prepared, from which it appears no valid grounds exist for the assumption that an insoluble trimethylcellulose exists, or that soluble trimethylcellulose is a disintegration product.

In one method of ethylcellulose manufacture<sup>6</sup>, the ethylated cellulose is purified by dissolving in hot water, filtering, and allowing precipitation to take place on cooling of the solution. The I. G. Farbenindustrie<sup>7</sup> also prepare etherified celluloses by treating partially alkylated cellulose

1. Ber. 1928, **61B**, 1982; abst. C. A. 1929, **23**, 5315; J. S. C. I. 1928, **47**, 1225-A; Chem. Zentr. 1929, I, 46.

2. K. Hess, C. Trogus and H. Friesse, Ann. Chem. 1928, **466**, 80; abst. C. A. 1929, **23**, 118; J. S. C. I. 1928, **47**, 1360-A; Chem. Zentr. 1929, I, 234.

3. Ann. Chem. 1926, **450**, 29; abst. C. A. 1927, **21**, 174; J. S. C. I. 1927, **46**, 44-A; Chem. Zentr. 1926, II, 2892.

4. Cellulosechemie, 1926, **7**, 73; abst. C. A. 1926, **20**, 3080.

5. Ann. Chem. 1928, **460**, 288; abst. C. A. 1928, **22**, 3635; J. S. C. I. 1928, **47**, 399-A; Chem. Zentr. 1928, I, 1848.

6. I. G. Farbenindustrie, Belg. P. 354784. Ital. P. 260746, 260707.

7. E. P. 292929; abst. J. S. C. I. 1929, **43**, 1011-B; Chem. Zentr. 1928, II, 1732. Addn. to E. P. 284298; abst. J. S. C. I. 1929, **43**, 593-B. F. P. 644480; abst. C. A. 1929, **23**, 480. F. P. Addn. 36578 to F. P. 644480; abst. C. A. 1930, **24**, 6013.

still containing unacted upon hydroxyl groups, with the halides of cyclicly substituted fatty acids or alicyclic carboxylic acids, thus producing mixed ethercellulose esters. In another process<sup>1</sup>, high-molecular carbohydrates as cellulose and starch, are treated with a gaseous alkylating agent (methyl or ethyl chloride) in the presence of moisture and less than 20 molecules of alkali hydroxide to 1 mol. of carbohydrate, calculated as  $C_6H_{10}O_5$ . During etherification the carbohydrate is kept in motion with a non-reacting gas which passes through a cooling arrangement to maintain uniform temperature in the autoclave.

While carbon bisulfide alone does not dissolve triethylcellulose to a clear solution<sup>2</sup>, a mixture of  $CS_2$  96 and acetone 4, with 7% triethylcellulose yields a film of thrice the extensibility and the same tensile strength as a film cast from pure acetone under the same conditions. Ethylcellulose may be worked up by dissolving at a high temperature in a solvent which does not dissolve the cellulose ether in the cold, e.g., benzene or ligroin, and the solution, after purifying while hot, is cooled, whereby the ethylcellulose separates. It may then be worked up into plastic masses while still wet by means of solvent at elevated temperature<sup>3</sup>.

To produce a high-grade knifing composition and mixed lacquers containing them<sup>4</sup>, cellulose ethers are admixed with inorganic fillers of a scaly, foliaceous or fibrous nature (graphite, mica, asbestos powder), and a finely divided organic filler (wood, flour, cork, lignite, cocoanut fiber), with the addition of volatile solvents and plasticizing bodies.

1. E. P. 302191; abst. J. S. C. I. 1929, **48**, 167-B. F. P. 640174; abst. C. A. 1929, **23**, 846; Chem. Zentr. 1928, II, 1616. Can. P. 283917.

2. E. P. 295942; abst. C. A. 1929, **23**, 2293; J. S. C. I. 1930, **49**, 99-B; Brit. Plastics, 1930, **1**, 446; Chem. Zentr. 1928, II, 2760. Belg. P. 350769.

3. E. P. 288143; abst. C. A. 1929, **23**, 513; J. S. C. I. 1929, **48**, 714-B; Plastics, 1929, **5**, 335; Brit. Plastics, 1929, **1**, 191; Silk J. 1928, **5**, #49, 80; Chem. Zentr. 1928, II, 304.

4. E. P. 302615; abst. C. A. 1929, **23**, 4307; J. S. C. I. 1929, **48**, 242-B; Chem. Zentr. 1929, I, 2371. E. P. 302616; abst. C. A. 1929, **23**, 4307; J. S. C. I. 1929, **48**, 242-B; Chem. Zentr. 1929, I, 2371.

Kieselguhr may also be added. Or<sup>1</sup> a varnish may be prepared, the groundwork being of a cellulose ether lacquer, superposed by a cellulose acetate or nitrocellulose solution, in which the solvents in the top coat are non-solvents of the cellulose ether used in the primary coat. Glycerol monoformal or other acetal type compound of a polyhydric alcohol<sup>2</sup> has received patent protection as a suitable high-boiler in cellulose ether and ester plastic combinations.

In the preparation of colored cellulose ether or ester plastics<sup>3</sup>, a method has been described whereby large quantities of coloring matters may be incorporated, provided they are in an exceedingly fine state of subdivision. If a cellulose ether, particularly ethylcellulose, is mixed with an alcohol of the terpene series<sup>4</sup>, (borneol, isoborneol, fenchol) especially in conjunction with a softening agent as benzyl alcohol or isobutyl phthalate, rapid gelatinization ensues, and valuable plastic combinations are alleged to result. Propyl, isopropyl or butyl naphthalenesulfonates<sup>5</sup> have also been put forward as desirable flexilizing agents for the cellulose ethers. The strength and elasticity of films and filaments of cellulose ethers is said to be augmented<sup>6</sup> by incorporating in the solution a cementing substance as linseed oil or a synthetic resin, or reactive substances as urea or hexamethylenetetramine. A bright yellow film suitable for use as a filter in photography may be formed from ethylcellulose to which is added an aldehyde resin produced from acetaldehyde and sodium hydroxide solution.

1. F. P. 642799; abst. C. A. 1929, **23**, 1517; Chem. Zentr. 1929, I, 3167.

2. I. G. Farbenind. A. G. E. P. 289523; abst. C. A. 1929, **23**, 704; J. S. C. I. 1928, **47**, 492-B; Chem. Zentr. 1928, II, 1282. Cf. E. P. 286789.

3. *Ibid.* E. P. 293485; abst. C. A. 1929, **23**, 1749; J. S. C. I. 1928, **47**, 668-B; Chem. Zentr. 1928, II, 1944. Cf. E. P. 247288.

4. *Ibid.* E. P. 295940; abst. C. A. 1929, **23**, 2293; J. S. C. I. 1930, **49**, 99-B; Br. Plastics, 1930, **1**, 446; Chem. Zentr. 1928, II, 2760. F. P. 659116; abst. C. A. 1929, **23**, 5283.

5. *Ibid.* F. P. 642220; abst. C. A. 1929, **23**, 1266.

6. *Ibid.* E. P. 293350; abst. C. A. 1929, **23**, 1750; Silk. J. 1928, 108; Chem. Zentr. 1928, II, 2206.

Artificial materials of any desired shape which are insoluble in water and organic media<sup>1</sup>, are made by mixing a solution of a cellulose ester which is insoluble and does not swell in water, with a cellulose ether dissolved in or swelled by water, and desiccating the emulsion so obtained. To produce water-resisting coloring on pellicles of cellulose ethers<sup>2</sup>, a solution of the ether containing the coloring matter is applied locally to a pellicle of cellulose acetate or ethylcellulose or regenerated cellulose. In the production of strips composed of cellulose derivatives carrying monochromatic or multi-colored figuring<sup>3</sup>, a 2% solution of nitrocellulose or acetylcellulose containing bronze powder is continuously sprayed on a travelling supporting surface through a stencil; and over this figuring when dry, is applied continuously a solution of 15% ethyl- or benzyl-cellulose in benzene-alcohol, colored with about 40% lampblack compared with the cellulose ether, a black film with sharply defined figurings of golden luster being obtained.

Medicinal ampoules are prepared by hermetically sealing open-ended tubes with a cellulose ether, which must be inert to the contents of the ampoule thus formed<sup>4</sup>. The seal may be perforated and the contents released drop by drop, at the time of use. In improving the strength of threads or films of cellulose ethers<sup>5</sup>, a synthetic resin is incorporated with the ether before film or filament formation. Ethylcellulose with a cresol formaldehyde condensate, or with urea-hexamethylamine condensate is advocated. The I. G. Farbenindustrie<sup>6</sup> have described the

1. I. G. Farbenind., E. P. 285355; abst. C. A. 1928, **22**, 4815; J. S. C. I. 1929, **48**, 677-B; Br. Plastics, 1929, **1**, 152; Chem. Zentr. 1928, I, 3016. Cf. E. P. 252176.

2. *Ibid.* E. P. 284999; abst. C. A. 1928, **22**, 4815; J. S. C. I. 1929, **48**, 637-B; Chem. Zentr. 1928, I, 2874.

3. *Ibid.* E. P. 288592; abst. J. S. C. I. 1929, **48**, 203-B; Chem. Zentr. 1928, II, 1154.

4. *Ibid.* E. P. 283952; abst. C. A. 1928, **22**, 4204.

5. *Ibid.* E. P. 294485; abst. C. A. 1929, **23**, 2032; Silk. J. 1928, Nov. 90; Chem. Zentr. 1929, I, 171; Kunst. 1929, **19**, 67.

6. *Ibid.* E. P. 296796; abst. C. A. 1929, **23**, 2540; J. S. C. I. 1928, **47**, 826-B; Chem. Zentr. 1929, I, 462. Cf. E. P. 247288.

formation of plasters, putties, knifing and filler compositions and lacquers comprising a dissolved cellulose ether admixed with graphite, talc, mica, asbestos, slag-wool, lithopone, white lead or ground slate, plasticizing agents being added.

In the preparation of packing material suitable for footwear<sup>1</sup>, cork cuttings combined with rubber, plasticized with tetrahydronaphthol acetate, ethylacetanilid, ethyl acetate and dibutyl carbonate. Mixed higher fatty acid esters and ethers of cellulose have been described<sup>2</sup> (as cellulose acetostearate and stearate, ethylcellulose laurate, cellulose caprate and caproate as celluloid substitutes and plastic-inducing components. Cellulose mono-, di-, and tri-caproate<sup>3</sup>; cellulose dinitrolaurate, dinitropalmitate, diacetolaurate, diaceto-palmitate<sup>4</sup>; cellulose di- and tri-palmitate<sup>5</sup>; cellulose mono-, di and tri-laurates, stearates and palmitates<sup>6</sup>; hydrocellulose distearate, dipalmitate and dilaurate<sup>7</sup>; cellulose mono-, di and tri-margarate<sup>8</sup>; cellulose monoacetyldilaurate, monoacetyldistearate<sup>9</sup>; and cellulose elaidate have been advocated to combine the tensile strength of cellulose acetate and ethylcellulose with the emollient effect of the cellulose fatty acid ester. Methyl-

1. I. G. Farbenind., E. P. 300924; abst. C. A. 1929, **23**, 4031; Chem. Zentr. 1929, I, 1529.

2. *Ibid.* E. P. 289063; abst. J. S. C. I. 1930, **49**, 185-B; Chem. Zentr. 1928, II, 511. F. P. 648154; abst. C. A. 1929, **23**, 2822. F. P. 35906 Addn. to F. P. 648154; abst. C. A. 1930, **24**, 4159.

3. H. Gault and P. Ehrmann, Caout. et Gutta. 1927, **24**, 13706; abst. C. A. 1927, **21**, 4062.

4. *Ibid.* Caout. et Gutta. 1927, **24**, 13824; abst. C. A. 1928, **22**, 1038; Plastics, 1927, 675.

5. *Ibid.* Caout. et Gutta. 1926, **23**, 13312, 13888; 1927, **24**, 13453; abst. C. A. 1927, **21**, 1350.

6. *Ibid.* Caout. et Gutta. 1927, **24**, 13532, 13603; abst. C. A. 1927, **21**, 2794.

7. *Ibid.* Compt. rend. 1923, **177**, 124; abst. C. A. 1923, **17**, 3249; J. S. C. I. 1923, **42**, 826.

8. P. Berthon, U. S. P. 1553924; abst. C. A. 1925, **19**, 3593; J. S. C. I. 1925, **44**, 877-B; Chem. Zentr. 1926, I, 1333. E. P. 201510; abst. C. A. 1924, **18**, 469; J. S. C. I. 1924, **43**, 128-B; Chem. Zentr. 1923, IV, 861; Faser. 1924, **6**, 46.

9. A. Gruen and F. Wittka, Zts. ang. Chem. Auf. 1921, **34**, 645; abst. C. A. 1922, **16**, 1566.

ethyl- or lauryl-cellulose may be obtained in pressed sheets or boards by compacting the alkalicellulose before etherification or esterification. In the preservation of wood<sup>1</sup>, cellulose laurate or laurylated starch, dissolved in methylene chloride has received patent protection.

Those higher fatty acid cellulose compounds as cellulose dilaurate<sup>2</sup>, may be prepared by the action of a higher fatty acid chloride (lauryl chloride) upon untreated cellulose in the presence of pyridine or quinoline. In the production of gelatinizing media for cellulose ethers and esters<sup>3</sup> products of sorbitol obtained by dehydration in the presence of such catalysts as active silica, carbon or aluminum oxide have been recommended. Polyhydroxy alcohols of the acetal type as glycoformal and glycerolmonoformal<sup>4</sup> are said to make excellent plasticizants for cellulose ethers, inducing pliability by virtue also of their normal slight deliquescence.

It has been found<sup>5</sup> that if a solution of a cellulose ether of about 8% and having about 2.5 ethyl groups per C<sub>6</sub> molecule is dissolved in a mixture of carbon bisulfide 84, ethyl ether 8, a film containing numerous small bubbles is formed when the film is cast at the usual temperature of about 24°, but when the same solution is worked up at 5°, a clear, lustrous, bubble-free film results. Ethylcellulose (2.5 ethyl groups) may be converted into technically useful thin films in a mixture of carbon bisulfide and ethyl ether when the solvent is in the ratio 5:1 for a 6% solution of ether; 95.5 for an 8%; and 90:10 for a 10% solution<sup>6</sup>.

1. I. G. Farbenindustrie A. G., E. P. 302698; abst. C. A. 1929, **23**, 4322; J. S. C. I. 1930, **49**, 559-B. E. P. 303168; abst. J. S. C. I. 1930, **49**, 559-B. Cf. E. P. 208685.

2. *Ibid.* E. P. 297766, Addn. to E. P. 283181; abst. J. S. C. I. 1929, **48**, 51-B; Chem. Zentr. 1929, I, 817.

3. *Ibid.* E. P. 301655, abst. C. A. 1929, **23**, 4282; J. S. C. I. 1929, **48**, 123-B; Chem. Zentr. 1929, I, 1506.

4. *Ibid.* E. P. 286789; abst. C. A. 1929, **23**, 513; J. S. C. I. 1928, **47**, 376-B; Chem. Zentr. 1928, I, 3016.

5. *Ibid.* E. P. 302667; abst. Silk. J. 1929, **5**, #59, 72; Kunst. 1931, **21**, 16; Chem. Zentr. 1929, I, 1875.

6. *Ibid.* E. P. 297676; abst. C. A. 1929, **23**, 2322; Chem. Zentr. 1929, I, 592.



Insulation suitable for wires is prepared by saturating paper or textile material with a solution of a cellulose ester or ether-ester of cellulose of a higher fatty acid<sup>1</sup> other than cellulose oleate, ethylcellulose palmitate or stearate being examples.

In the manufacture of cellulose ethers, after removal of the associated air by passing a current of gas or vapor capable of being absorbed by alkali over the carbohydrate material<sup>2</sup> contained in a vessel under vacuum, the alkali compound is formed by treatment with caustic soda and etherification completed in the usual manner, or<sup>3</sup> a current of gas or vapor which is absorbed on access of the esterifying liquid, is passed through a vessel containing a vacuum until the associated air is eliminated.

Colored masses and lacquers of cellulose ethers and artificial or natural resins are prepared<sup>4</sup> with salts formed by dyes containing sulfonic or carboxylic groups with organic derivatives of ammonia in which the N atoms are not bound to such a C atom as is itself directly connected with 2 atoms of N. Suitable bases are alkylamines (ethylamine, di- and tri-ethanolamine), aralkyl- and aryl-amines (cyclo- and dicyclo-hexylamine), heterocyclic bases (pyridine, piperidine, quinoline), and bases of the triphenylmethane dye classes.

A process has been described<sup>5</sup> for dyeing cellulose ethers with water-soluble dyestuffs, by effecting the dyeing process in the presence of hydrogenated isocyclic bases (hexahydroaniline, hexahydromethylaniline, hexahydro-ethylaniline, hexahydrotoluidine, hexahydroethyl-o-tolui-

1. I. G. Farbenind., E. P. 297749; abst. C. A. 1929, **23**, 2772; Br. Plastics, 1930, **1**, 448; J. S. C. I. 1930, **49**, 21-B.

2. *Ibid.* E. P. 293316; abst. C. A. 1929, **23**, 1750; J. S. C. I. 1929, **48**, 1011-B; Chem. Zentr. 1928, II, 1840. D. R. P. 492246; abst. C. A. 1930, **24**, 2469.

3. *Ibid.* E. P. 293757 Addn. to E. P. 293316; abst. J. S. C. I. 1929, **48**, 1011-B; Chem. Zentr. 1928, II, 2060.

4. *Ibid.* E. P. 293067; abst. C. A. 1929, **23**, 1517; J. S. C. I. 1928, **47**, 681-B; Chem. Zentr. 1928, II, 2072.

5. *Ibid.* E. P. 293766; abst. C. A. 1929, **23**, 1759; J. S. C. I. 1930, **49**, 185-B; Chem. Zentr. 1928, II, 2064.

dine, hexahydroxydiline or hydrogenated 1.5-naphthalenediamine). In the formation of colored brushwork lacquers<sup>1</sup>, water-insoluble cellulose ethers are dissolved in glycol mono- or di-alkyl ethers (glycol monoethyl ether) or their esters, and the resulting lacquers diluted with aromatic hydrocarbons (tetrahydronaphthalene, oil of turpentine) or their halogen derivatives (monochlor-benzene, -toluene, -xylene). The products give highly glossy coatings when dry.

Cellulose ether or ester filaments may be dyed with azo dyes obtained by coupling 1.3-diketohydrindene with diazotized arylamine- monosulfonic or -monocarboxylic acids, sulfanilic acid (yellow), anthranilic acid (yellow), or 2-amino-6-naphthoic acid. Cellulose ethers are dyed with an azo dye obtained by coupling a diazotized dinitroaminophenol with an unsulfonated and uncarboxylated aminonaphthol<sup>2</sup>. Brownish violet to black dyeings are obtained fast to washing, the fastness of which is improved by diazotizing and developing on the fiber.

To produce resist effects in dyeing with vat dyes<sup>3</sup>, the fabric is printed with a resist paste containing an oxidizing agent (sodium *m*-nitrobenzenesulfonate or sodium bichromate) and a water-soluble cellulose ether, dried, and dyed in the usual manner in a hot alkaline solution of a vat dye. A suitable paste consists of a 15% aqueous solution of methylcellulose, and sodium *m*-nitrobenzenesulfonate. Plastifiable substances of a cellulose ether base<sup>4</sup> are colored by incorporating therein copper or chromium compounds of 4-chlor-2-aminophenol-5-sulfonate, diazotized with 1-phenyl-3-methyl-5-pyrazolone, or the mass may be

1. I. G. Farbenind., E. P. 294158; abst. J. S. C. I. 1928, **47**, 719-B; Cf. E. P. 247288, 293485; abst. J. S. C. I. 1926, **45**, 315; 1928, **47**, 668.

2. *Ibid.* E. P. 290720; abst. C. A. 1929, **23**, 994; J. S. C. I. 1928, **47**, 521-B. F. P. 629097; abst. Chem. Zentr. 1928, I, 756.

3. *Ibid.* E. P. 290177; abst. J. S. C. I. 1929, **48**, 849-B; Chem. Zentr. 1928, II, 1945.

4. *Ibid.* F. P. 634457; abst. C. A. 1928, **22**, 3747; Chem. Zentr. 1928, I, 2679; Kunst. 1929, **19**, 140.

dyed with a monoazo dye<sup>1</sup> produced by coupling a diazo compound of the benzene or naphthalene series, as *p*-cresol with *p*-phenylenediamine or *p*-phenylenediamine-*o*-sulfonate.

Dinitroarylamino-diarylamine dyes suitable for coloring the cellulose ethers result by condensing *p*-aminodiphenylamine with 4-halo-1,3-dinitro-6-X-benzene or 4-halo-3,5-dinitro-1-X-benzene, where X may be carboxyl or substituted carboxyl. The products dye cellulose ethers yellow to brown-red. A cellulose ether dye<sup>2</sup> is also formed by coupling non-sulfonated aromatic diazo compounds with 2,4-diaminophenylmethanesulfonic acid. Thus (aminoazobenzene gives a straw-yellow, 4-nitroso-1-aminobenzene a Corinth, and 1-aminoazonaphthalene an orange. The straw color produced on cellulose ester or ether silk by amino-benzeneazo-2,4-diaminophenylmethanesulfonic acid<sup>3</sup>, is turned to a red-brown. Cellulose ethers are also dyed yellow diazobenzene. The orange color obtained from 1-amino-naphthaleneazo-2,4-diaminophenylmethanesulfonic acid is turned to a red-brown. Cellulose ethers are also dyed yellow with monosulfoarylazodiarylamine containing at least one nitro group in the diarylamine complex<sup>4</sup>. Examples are 4-benzeneazo-2,6-dinitro-4'-sulfodiphenylamine and 4-benzeneazo-4'-nitro-2-sulfodiphenylamine.

When diazotized *p*-aminoacetanilide is coupled with *p*-cresol<sup>5</sup>, a yellow powder results, suitable for dyeing the cellulose ethers. The acetyl group may be split off by heat-

1. I. G. Farbenind., U. S. P. 1765142; abst. J. S. C. I. 1930, **49**, 945-B; 1931, **50**, 763-B; C. A. 1930, **24**, 4171. E. P. 269934; abst. J. S. C. I. 1928, **47**, 121-B; C. A. 1928, **22**, 1482; Chem. Zentr. 1927, II, 1092. D. R. P. 469514; abst. C. A. 1929, **23**, 1287; Chem. Zentr. 1929, I, 1274. F. P. 632887; abst. C. A. 1928, **22**, 3535.

2. *Ibid.* D. R. P. 467036; abst. C. A. 1929, **23**, 527; Chem. Zentr. 1929, I, 303.

3. *Ibid.* D. R. P. 468210, Addn. to D. R. P. 467036; abst. C. A. 1929, **23**, 717; Chem. Zentr. 1929, I, 303. D. R. P. 467036; abst. C. A. 1929, **23**, 527.

4. *Ibid.* D. R. P. 468981; abst. C. A. 1929, **23**, 994. E. P. 275230, 284652; C. A. 1928, **22**, 4834.

5. *Ibid.* Swiss P. 126200; abst. C. A. 1929, **23**, 715. E. P. 270351; abst. C. A. 1928, **22**, 1692; Chem. Zentr. 1927, II, 1094.

ing with caustic soda<sup>1</sup>, producing other desirable cellulose ether dyes. The finely divided state of freshly precipitated insoluble or difficulty soluble dyes is preserved by pasteing them with an alkylcellulose, an illustrative example being the treatment with methylcellulose with azo dyes from 2-hydroxy-3-naphthoic acid anilid and diazotized 4-nitro-2-aminobenzoic acid methyl ester; and *b*-naphthol diazotized with 3-nitro-4-aminotoluene<sup>2</sup>.

Glyceryl formate, and glycol mono- and di-formates<sup>3</sup> have been put forward as solvents for benzylcellulose and shellac. A photographic raw film has been described with visible reproducible inscriptions<sup>4</sup> in which the inscription is protected from injury by the application thereto of a lacquer of benzylcellulose in a mixture of acetone and benzene<sup>5</sup>.

In the treatment of black gunpowder<sup>6</sup>, the speed of combustion is retarded by coating each grain with a film of ethyl- or benzyl-cellulose, or cellulose acetate. P. Joliot diminishes the inflammability of filaments from cellulose derivatives by incorporating therewith in solution<sup>7</sup>, such bodies as borax or tin silicophosphate. The cellulose ether filament may be freed from oil by a treatment in the cold with a solvent as tetrachlorethane, ethylene chloride, carbon bisulfide or ethyl ether.

1. I. G. Farbenind., Swiss P. 127714; abst. C. A. 1929, **23**, 1281. E. P. 270351; abst. C. A. 1928, **22**, 1692; Chem. Zentr. 1927, II, 1094.

2. *Ibid.* Swiss P. 127223; abst. C. A. 1929, **23**, 1286. E. P. 269918; abst. C. A. 1928, **22**, 1480; J. S. C. I. 1928, **47**, 666-B; Chem. Zentr. 1927, II, 1096.

3. *Ibid.* Swiss P. 127241; abst. C. A. 1929, **23**, 1190; Chem. Zentr. 1929, I, 120.

4. *Ibid.* E. P. 295578; abst. C. A. 1929, **23**, 2113; J. S. C. I. 1929, **48**, 912-B; Chem. Zentr. 1929, I, 184.

5. *Ibid.* E. P. 287124; abst. J. S. C. I. 1928, **47**, 914-B; Chem. Zentr. 1928, I, 3144.

6. Imperial Chemical Industries, E. P. 300611; abst. J. S. C. I. 1929, **48**, 912-B.

7. P. Joliot, F. P. 639196; abst. C. A. 1929, **23**, 705; Chem. Zentr. 1929, II, 2523. F. P. 35500 Addn. to F. P. 639196; abst. C. A. 1930, **24**, 3912.

In the confectionery and sweetmeats industry<sup>1</sup> the plaques, bands or like dropping-material is formed of, or provided with a coating of ethyl- or benzyl-cellulose, the ether being applied as a liquid to a base for backing, usually of paper. Kalle & Co.<sup>2</sup> prepare anaglyphs based on the discovery that uniform results are attainable in an inexpensive manner by using layers containing stable diazo compounds such as are decomposed by the action of light, the support or base for the layer being a cellulose ether film, or paper coated with cellulose ether or ester<sup>3</sup>. They dye cellulose ether filaments with azo dyes prepared from nitrated hydroxydiazo compounds and aromatic amines or phenols. As examples, diazotized picramic acid and *b*-naphthylamine gives yellow shades, violet with *a*-naphthylamine, orange with *m*-phenylenediamine, and brown with *a*-naphthol.

In a study of the shape of molecules of cellulose and its derivatives by spreading them out in a mono-molecular layer<sup>4</sup>, J. Katz and P. Samwel found that cellulose ether in chloroform solution spreads rapidly on water, and gives a mon-molecular layer upon evaporation of the solvent, the film being slightly compressible. Its surface and thickness have been determined at several pressures. For ethylcellulose high, low or medium viscosity or in crystalline form was found from 60-66.5 sq. A. U. surface, 5.3-5.55 A. U. thickness; for methylcellulose (also 4 types) 59-61 and 4.1-4.3; for triacetylcellulose, 37.5-40.5 and 8.15-8.9.

M. Klein<sup>5</sup> has illustrated constructional details for a cellulose ether spinning apparatus, in which each cell is subdivided by one or more diaphragms into an upper zone

1. J. Jörgensen, E. P. 288758.
2. E. P. 301490; abst. J. S. C. I. 1930, **49**, 38-B. Compare König, *Farbenfotografie*, Berlin, 1921, 65.
3. D. R. P. 469513; abst. C. A. 1929, **23**, 1288; Chem. Zentr. 1929, I, 2112.
4. *Naturwissenschaften*, 1928, **16**, 592; abst. C. A. 1928, **22**, 3986; J. S. C. I. 1928, **47**, 937-A; Chem. Zentr. 1928, II, 963.
5. U. S. P. 1767216; abst. J. S. C. I. 1930, **49**, 761-B. E. P. 292561; abst. J. S. C. I. 1929, **48**, 595-B; Chem. Zentr. 1928, II, 1407.

containing the spinning nozzle and lower heating zones where aspiration is effected and which are successively traversed by the spun thread. Or<sup>1</sup>, the spinning jet is provided with an inlet for cold air in its upper part where the downwardly directed spinning nozzle is situated, the thread issuing therefrom passing down a vertical passage between diaphragms, set obliquely in the cell. In a modification of the above<sup>2</sup>, each zone of the cell has its own inlet and outlet.

Kodak, Ltd.<sup>3</sup>, have described a folding screen composed of ethylcellulose with suitable plastifiers. A. Landucci<sup>4</sup> dissolves a cellulose ether or ester in an organic solvent miscible with water, precipitates in an aqueous bath, the opaque product being rendered transparent by treatment with acetone or similar solvent.

F. Lange<sup>5</sup> prepares carbohydrate depolymerization products, by treatment of cellulose or starch with ethylene glycol or monochlorhydrin at boiling temperature. In order to serve as a distinguishing characteristic in various temporary operations<sup>6</sup>, artificial yarns and threads obtained by the dryspinning of cellulose ethers are dyed a fugitive color (as by Carmine blue or Brilliant carmine). In the permanent dyeing of cellulose ether and ester

1. U. S. P. 1716781; abst. C. A. 1929, **23**, 3808; J. S. C. I. 1929, **48**, 773-B. E. P. 292608; abst. J. S. C. I. 1929, **48**, 774-B; Chem. Zentr. 1928, II, 1407. F. P. 648397; abst. C. A. 1929, **23**, 3099.

2. E. P. 300166; abst. C. A. 1929, **23**, 3574; J. S. C. I. 1929, **48**, 893-B; Silk. J. 1929, **5**, #57, 74; Chem. Zentr. 1929, I, 1169. F. P. 686027; abst. C. A. 1930, **24**, 6015.

3. F. P. 636905.

4. U. S. P. 1658725; abst. C. A. 1928, **22**, 1237; J. S. C. I. 1928, **47**, 295-B; Chem. Zentr. 1928, I, 2028; Kunst. 1929, **19**, 161.

5. U. S. P. 1714565; abst. C. A. 1929, **23**, 3543; J. S. C. I. 1929, **48**, 936-B; Chem. Zentr. 1929, II, 1747. E. P. 290377; abst. C. A. 1929, **23**, 981; J. S. C. I. 1928, **47**, 515-B; Chem. Zentr. 1928, II, 1818.

6. G. Lardy, U. S. P. 1693759; abst. C. A. 1929, **23**, 996; J. S. C. I. 1929, **48**, 51-B; Chem. Zentr. 1929, II, 1993. E. P. 251580; abst. J. S. C. I. 1926, **45**, 975-B; Rev. Gen. Mat. Plast. 1927, #1, 45; Chem. Zentr. 1927, I, 1251. D. R. P. 480899; abst. C. A. 1929, **23**, 5048; Chem. Zentr. 1929, II, 1993. F. P. 597394; abst. Chem. Zentr. 1926, I, 1743. Swiss P. 123891; abst. Chem. Zentr. 1928, I, 2147. Swiss P. 131327.

yarns<sup>1</sup>, green shades fast to alkalis are obtained by salts as oxalates of unsulfonated triarylmethane derivatives, such as 2,4-dimethyl derivatives of malachite green obtained by oxidizing the product of condensation of 4,4'-tetramethyldiaminobenzohydrol with *m*-xylene.

In making ethylcellulose in a "one step" operation, O. Leuchs and E. Dörr<sup>2</sup> remove water during the progress of etherification with simultaneous adding of caustic alkali to the ethylation mixture, ethyl chloride being used. Solid NaOH is used for water absorption. T. Lieser<sup>3</sup> has described the preparation of "pure" sodium xanthate, and products obtained therefrom by etherification with methyl sulfate and methyl iodide.

L. Lilienfeld has described<sup>4</sup> cellulose urethanes and bodies obtained therefrom in which at least one hydrogen atom of the amido group is replaced by an alcohol radical, which give strong films and filaments when precipitated from their solutions by inorganic acids (sulfuric acid 40-78%, phosphoric acid 45-70%, or hydrochloric acid 20-35% strength). He has also patented cellulose compounds with monohalogen fatty acid, obtained by treating cellulose and alkali with monochlor-, monobrom- or monoiodo-acetic or -propionic acid<sup>5</sup>. Other valuable properties arise<sup>6</sup>, if in the manufacture of these compounds, not over 0.5 molecular proportion of monohalogen fatty acid per molecule of alkali is used.

1. L. Lawrie, F. Linch and E. Rodd, U. S. P. 1772515; abst. J. S. C. I. 1930, **49**, 944-B. E. P. 297897; abst. C. A. 1929, **23**, 2836; J. S. C. I. 1928, **47**, 891-B; Chem. Zentr. 1929, I, 1274. F. P. 655948; abst. C. A. 1929, **23**, 4084. D. R. P. 529692.

2. U. S. P. 1694127; abst. C. A. 1929, **23**, 981; J. S. C. I. 1929, **48**, 353-B; Plastics, 1929, **5**, 454; Chem. Zentr. 1929, I, 1635. E. P. 306857; abst. J. S. C. I. 1929, **48**, 353-B. D. R. P. 505797; abst. C. A. 1931, **25**, 592.

3. Ann. 1928, **464**, 43; abst. J. S. C. I. 1928, **47B**, 742; C. A. 1928, **22**, 4792.

4. U. S. P. 1674403; abst. J. S. C. I. 1928, **47**, 853-B. See E. P. 231806.

5. U. S. P. 1682292; abst. J. S. C. I. 1928, **47**, 744-B. See E. P. 231809.

6. U. S. P. 1682294; abst. J. S. C. I. 1928, **47**, 744-B. See E. P. 231809.

In coating pigmented compositions comprising cellulose ethers or esters<sup>1</sup>, livering or jelling is prevented by adding 0.1-0.5% of substances such as oxalic, phosphoric, tartaric, citric, malic, formic, boric or acetic acids<sup>2</sup>. In order to obtain a dull luster on ether silk or acetate silk<sup>3</sup>, the "dry" evaporation process after filament formation, is carried out by injecting steam in the spinning chamber or leading a thread not completely freed from solvent into a chamber containing steam. In the production of phonograph records and other molded blocks<sup>4</sup>, E. Noack combines bitumen or asphalt with cellulose ethers and esters with the addition of ethyl lactate, triacetin, sulfanilid and triphenyl phosphate as plastic-inducers. Pathe Cinema<sup>5</sup> have published a formula for plastic cellulose ethers, composed of triphenyl phosphate 15 to tricresyl phosphate 12, with benzylcellulose. In artificial leather manufacture<sup>6</sup>, cellulose ethers are kneaded, preferably *in vacuo*, with named softening agents to a semi-solid state, then rolled out to a thin layer, placed on a fabric or paper base, heated, and drawn between friction pressure rollers to produce a unitary material.

In one patented method for reducing the viscosity characteristics of the cellulose ethers<sup>7</sup> small amounts of acetic or hydrochloric acids are allowed to act upon a solution of the ether, until the viscosity has been reduced by at least a third. M. Renkers produces tracing-cloth<sup>8</sup> by treating the

1. J. McBurney and E. Nollau. E. P. 278696; abst. C. A. 1928, **22**, 2673; J. S. C. I. 1928, **47**, 866-B; Chem. Zentr. 1928, I, 989.

2. In this connection see E. Worden, Nitrocellulose Industry, 1911, 389.

3. Naamløoze Vennootschap Nederlandsche Kunstzijdefabriek, F. P. 640446; abst. C. A. 1929, **23**, 982; Kunst. 1929, **19**, 163.

4. E. P. 290801; abst. C. A. 1929, **23**, 943; Plastics, 1929, 574; Kunst. 1929, **19**, 138; Chem. Zentr. 1928, II, 1283.

5. F. P. 643884; abst. C. A. 1929, **23**, 1749; Chem. Zentr. 1929, I, 2602.

6. W. Plinatus, E. P. 301759; abst. C. A. 1929, **23**, 4369; J. S. C. I. 1930, **49**, 319-B; Chem. Zentr. 1929, I, 1875. See E. P. 317824.

7. C. Prachel and L. Branchen, U. S. P. 1679943; abst. C. A. 1928, **22**, 3777; Plastics, 1929, 26; J. S. C. I. 1928, **47**, 810-B; Chem. Zentr. 1928, II, 1639. See U. S. P. 1548938, 1635013, 1679966.

8. M. Renker, E. P. 297993; abst. J. S. C. I. 1928, **47**, 889-B; Chem. Zentr. 1929, I, 1299.



cloth with a solution of cellulose ethers or esters in a solvent which does not dissolve the fats and oils used in finishing the cloth, e.g. methyl glycol, methylglycollic acetate, ethyl glycol, ethylglycolic acetate.

Allylcelluloses have been described by I. Sakurada<sup>1</sup> obtainable by treating tissue paper with 40-50 volumes of sodium hydroxide solution and allyl bromide, the higher allylcelluloses (di- and tri-ether of C<sub>6</sub> unit) being directly obtained. The higher allylcellulose is partly soluble in alcohol, benzene and carbon hexachloride. Diallylcellulose tetrabromide was isolated in almost pure state. J. Schindelmeyer<sup>2</sup> claims to be the first to use esters of borneol, isoborneol and terpeneol (formates, acetates, butyrates, phthalates, salicylates) in paint and varnish compositions containing cellulose ethers.

F. Schmidt<sup>3</sup> has reviewed the preparation and properties of commercially important plastic materials containing cellulose ethers and esters. In the methylation of starch, L. Schmid and M. Zentner<sup>4</sup> found that potato starch after 27 methylations with diazomethane yields a methylated starch containing 21.5% methoxyl, unchanged by further methylation. G. Schneider<sup>5</sup> produces metallic effects by rubbing crystals of metallic salts on polished surfaces of cellulose derivatives as ethers or esters, these being preserved by coating with another cellulose compound in solution, in which the solvent of the latter does not dissolve the former cellulose compound. Example, cellulose acetate in acetone, followed by ethylcellulose in benzene.

1. J. S. C. I. (Japan) 1928, **31**, 638; Suppl. Binding, 1928, **31**, 157-B; abst. C. A. 1929, **23**, 3081; J. S. C. I. 1929, **48**, 299-B. Bull. Inst. Phys. Chem. Research (Tokyo), **8**, 114; Abstract Ed. **2**, 18; abst. C. A. 1929, **23**, 3572; J. S. C. I. 1929, **48**, 430, 799-A; Zts. ang. Chem. 1929, **42**, 549.

2. E. P. 283619; abst. J. S. C. I. 1928, **47**, 237-B; Chem. Zentr. 1928, **1**, 2028.

3. Kolloid Zts. 1928, **46**, 324; abst. J. S. C. I. 1929, **48**, 125-B.

4. Monatsh. 1928, **49**, 111; abst. J. S. C. I. 1928, **47**, 742-A; C. A. 1928, **22**, 3395.

5. Can. P. 277599; abst. C. A. 1928, **22**, 2840. See E. P. 274841.

In improvements relating to duplicating stencils<sup>1</sup>, Yoshino paper is coated with a composition which includes cellulose ethers or nitrated cellulose ethers, and softeners (casein, glycerol, palmitic acid, sodium oleate). The P. Smith<sup>2</sup> stencil blank is similar. Powdered plastic material may be prepared by mixing a cellulose ether or ester with a plasticizer, the whole being precipitated and then worked up in the damp state<sup>3</sup>. Cellulose ethers and esters may be colored<sup>4</sup> by means of lakes of organic coloring matters which are sparingly soluble in water or alcohol, by incorporating them first with the cellulose derivatives, eosine with lead acetate being illustrative. In cellulose ether filament formation, barium sulfate in impalpable powder may be added to the solution before spinning to induce a subdued luster in the filaments<sup>5</sup>.

A decorative effect is obtainable on plastic sheets of methyl-, ethyl- and benzyl-cellulose<sup>6</sup>, by uniting one or more colored or decorative cloths made of threads of cellulose material which is plastic when heated, to the sheet so that the structure of the cloth disappears completely upon application of pressure. In the manufacture of compound transparent glass sheets<sup>7</sup>, the central layer between the glass is composed of methyl- or ethyl-cellulose or caroubin, all of which tend to *bleach*, not *darken* on exposure to light.

1. H. Simon, E. P. 286466; abst. C. A. 1929, **23**, 249; Chem. Zentr. 1928, I, 2767.

2. U. S. P. 1655249.

3. Soc. Chim. des Usines du Rhone, E. P. 285829, Addn. to E. P. 275558; abst. J. S. C. I. 1929, **48**, 167-B.

4. Soc. Chim. des Usines du Rhone and M. Theumann, E. P. 294137; Addn. to E. P. 275553; abst. C. A. 1929, **23**, 2046; J. S. C. I. 1928, **47**, 783-B; Chem. Zentr. 1928, II, 2421. M. Theumann, U. S. P. 1789122; abst. C. A. 1931, **15**, 1101; Chim. et Ind. 1921, **25**, 957; Plastics, 1931, **7**, 297.

5. Soc. Chim. des Usines du Rhone, E. P. 294623; abst. J. S. C. I. 1929, **48**, 596-B; Silk J. 1928, Dec. 76; Chem. Zentr. 1928, II, 2206.

6. Soc. des Usines Chim. Rhone-Poulenc, E. P. 305189; abst. C. A. 1929, **23**, 4819; Chem. Zentr. 1929, II, 238. F. P. 648152; abst. C. A. 1929, **23**, 2793. D. R. P. 530121.

7. Soc. d'Etude des Verres et Glaces de Surete, E. P. 293052; abst. J. S. C. I. 1929, **48**, 323-B; Chem. Zentr. 1929, I, 282.

Cellulose ether and ester dyestuffs dyeing blue<sup>1</sup> are formed by causing 1-oxy-4-aminoanthraquinone or a 1.4-diaminoanthraquinone to interact with an aromatic diamine (phenylenediamine, naphthylenediamine, benzidine), there being produced 1-aryldio-4-aminoanthraquinones. Or<sup>2</sup>, fast blue to green tints result on cellulose ethers by dyeing with tetraminoanthraquinones having one or two of the amino groups substituted by an aryl residue, an example being 1.5-diamino-4.8-diphenylaminoanthraquinone. In discharging dyed cellulose ether or ester filaments<sup>3</sup>, animal charcoal having high absorbing properties is used, with or without the addition of swelling agents to augment the receptivity of the cellulose compound for the charcoal.

Last traces of volatile solvent are removable from freshly prepared cellulose ether films by passing the film under slight tension through a tunnel into which low-pressure steam is continually introduced<sup>4</sup> in sufficient quantity to maintain a damp atmosphere without actually wetting the film. Or the film<sup>5</sup> may be passed through a 0.5-1% solution of caustic soda or sodium hydrogen sulfate, the whole being electrically earthed. In this way, danger of sparking and ignition of the volatile solvent is avoided. Knitted or woven fabrics<sup>6</sup> may be repaired and mended by attaching thereto patches made of cellulose ester or ether fabrics, heat and pressure afterwards being applied.

1. Soc. Chem. Ind. Basle, E. P. 285096; abst. C. A. 1928, **22**, 4832; J. S. C. I. 1929, **48**, 674-B; Chem. Zentr. 1928, I, 3119. D. R. P. 501020; abst. C. A. 1930, **24**, 4639.

2. *Ibid.* E. P. 293006; abst. C. A. 1929, **23**, 1514; Silk J. Sept. 1928, 50; J. S. C. I. 1929, **48**, 849-B; Chem. Zentr. 1928, II, 2064. F. P. 656057; abst. C. A. 1929, **23**, 4083. See E. P. 271898.

3. Soc. Pour La Fabrikation de la Soie "Rhodiaseta," E. P. 297186; abst. C. A. 1929, **23**, 2580; J. S. C. I. 1928, **47**, 855-B; Chem. Zentr. 1929, I, 579. F. P. 647865; abst. C. A. 1929, **23**, 2582; Chem. Zentr. 1929, I, 1636.

4. Spicers, Ltd., and H. Hands, E. P. 287635; abst. J. S. C. I. 1928, **47**, 444-B. F. P. 659387; abst. C. A. 1929, **23**, 5317. Can P. 281686. Belg. P. 347045.

5. Spicers, Ltd., and H. Hands, E. P. 301439; abst. J. S. C. I. 1929, **48**, 203-B; Chem. Zentr. 1929, I, 2004. F. P. 645912; abst. C. A. 1929, **23**, 2293.

6. W. Stelkens and C. Liedtke, E. P. 302858; abst. C. A. 1929, **23**, 4353.

R. Thenoz<sup>1</sup> has formulated a device for stretching artificial threads from cellulose ether and ester solutions during spinning, the device being provided with a pair of drawing rollers rotating counter-clockwise and adjustable in such a manner as to control the extent of drawing-action. He has also patented an arrangement for spinning solutions<sup>2</sup>, whereby a rotatory twist is imparted to the filament, and has provided a die<sup>3</sup> with a conduit for circulation of a temperature-controlling fluid to increase uniformity in filament denier obtained. M. Theumann<sup>4</sup> produces lakes and pigmented products directly in the dissolved cellulose ether or ester solution by adding an inorganic salt thereto (ferric chloride), and an acetone or other solution of a precipitant (potassium ferricyanide, as example).

G. Trümpler<sup>5</sup> pressure-molds materials by taking finely divided cellulose ethers or esters with one or more volatile liquids which are non-solvents, but plasticizers, which are compacted by a combination of pressure and boiling water, hot salt solutions or superheated steam. Or<sup>6</sup>, quick-drying, non-porous, and non-clogging surfacing or stopping pastes for coating metal, wood or similar surfaces, result when one or more cellulose ether or esters, to which resins and finely divided metals may be added, are incorporated therewith.

In the methylation of beech wood<sup>7</sup>, 5-7 methylations gave a maximum methoxyl of 39.-39.4%, the product not changing in solvents of methylcellulose and lignin, does not

1. E. P. 283139; abst. C. A. 1928, **22**, 3990; Silk J. 1928, **4**, #48, 64.

2. E. P. 283140; abst. C. A. 1928, **22**, 3990.

3. R. Thenoz and H. Barthelemy, E. P. 293416; abst. C. A. 1929, **23**, 175; Silk J. 1928, **5**, #54, 88.

4. U. S. P. 1789121; abst. C. A. 1931, **25**, 1101; *Plastics*, 1931, **7**, #5, 277; *Chim. et Ind.* 1931, **25**, 956. Can. P. 278978; abst. C. A. 1928, **22**, 2839.

5. E. P. 294251; abst. J. S. C. I. 1930, **49**, 53-B; *Brit. Plastics*, 1930, **1**, #10, 447; *Chem. Zentr.* 1928, II, 2205.

6. E. P. 294262; abst. C. A. 1929, **23**, 2050; J. S. C. I. 1929, **48**, 1023-B. F. P. 668123; abst. C. A. 1930, **24**, 1529.

7. A. von Wacek, *Ber.* 1928, **61B**, 1604; abst. C. A. 1928, **22**, 4808; J. S. C. I. 1928, **47**, 1227-A; *Can. Pulp & Paper Mag.* 1929, Aug. 1, 187; *Chem. Zentr.* 1928, II, 2644.

swell, and hardly dissolves in traces. Upon hydrolysis, a product was obtained of 40.3-43.2% methoxyl, corresponding to trimethylcellulose mixed with 41-18.8% dimethylcellulose. Since this trimethylcellulose does not dissolve before hydrolysis, the conclusion is drawn that the cellulose operated upon is not combined through its three hydroxyl groups in the good. G. Whitby<sup>1</sup> has reviewed work on the higher cellulose esters and cellulose ethers.

To increase the impermeability to water of articles composed of regenerated cellulose, or cellulose ethers which are non-resistant to water<sup>2</sup>, the articles are treated, in the presence of a plasticizer if desired, with a water-miscible swelling liquid (diamyl phthalate in formic or acetic acids) and afterwards coated with a cellulose ester (nitrocellulose) with which the swelling liquid is compatible. F. Wood and A. Alexander in a study of the preferential absorption of alkali by partially methylated cellulose by the centrifuge method<sup>3</sup>, and of the heat evolved during the process, have determined that the greater dispersion of the methylated cellulose results in a great increase in the heat evolution (for anhydrous materials).

In a series of two patents, G. Zelger has added to the number and complexity of the phosphoric compounds of phenol, cresol and naphthol by describing the use with ethyl- and benzyl-cellulose as plastifying bodies, phosphates of monomethyldiphenyl, monoethyldiphenyl, dimethylmonophenyl, diethylmonophenyl<sup>4</sup>, and monomethyl di(monochlorphenyl), monomethylmonophenylmonochlorphenyl, dimethylmonochlorphenyl, dimethylmono(dichlorphenyl), and diethylmonochlorphenyl<sup>5</sup>.

1. Fourth Colloid Symposium Monograph, 1926, 203; abst. C. A. 1927, **21**, 3293; J. S. C. I. 1928, **47**, 17-A; Chem. Zentr. 1928, II, 856.

2. Wolff & Co., and R. Weingand, E. P. 298605; abst. C. A. 1929, **23**, 3097; J. S. C. I. 1930, **49**, 237-B; Chem. Zentr. 1929, I, 958. See E. P. 245683, 257924, 262440, 273564, 274054, 276206, 277309, 298609, 304717.

3. J. S. C. I. 1928, **47**, 357-T; abst. C. A. 1929, **23**, 3578; Chem. Zentr. 1929, I, 1065.

4. U. S. P. 1685443; abst. J. S. C. I. 1929, **48**, 242-B.

5. U. S. P. 1685444; abst. J. S. C. I. 1929, **48**, 242-B; Chem. Zentr. 1929, I, 171.

In the manufacture of patterned or effect materials having a base of cellulose ethers<sup>1</sup> a molding powder composed of the ether and a plasticizing agent is placed in contact with a colored fabric and the material united by combined heat and pressure. In the drying of cellulose ether filaments when made by the wet spinning method<sup>2</sup>, the filaments after emergence from the precipitating bath are conducted through a drying cell wherein a counter-current of heated air removes the moisture.

It is claimed that mordanting and weighting cellulose ether filaments may be carried on simultaneously by treating them in the swollen or unswollen state with zinc chloride solution<sup>3</sup>. An azo dye has been described as especially applicable to the tinting of cellulose ethers<sup>4</sup>, obtained by coupling 4,6-dinitro-2-amino-1-hydroxybenzene with 1-amino-8-hydroxynaphthalene in the presence of an acid-binding agent. The product is soluble in water and dyes black shades, which are intensified if the dye is diazotized on the fiber and developed with 2,4-tolylenediamine.

Cellulose ether filaments are dyed with water-soluble monazo dyes obtained by coupling a diazotized dinitro-*o*-aminophenol with aminonaphthols containing no sulfonic or carboxylic groups<sup>5</sup>. Examples, 4,6-dinitroaminophenol with 1,8-, or 1,6-, or 2,8- or 1,5-aminonaphthol (black to violet brown giving blacks to deep browns by diazotization and development on the fiber); partially reduced 2,4,6-trinitro-*m*-cresol gives similar shades. 4,6-Dinitro-*o*-aminophenol with 1,8-aminonaphthol is especially recommended.

1. W. Dickie and J. Rooney, U. S. P. 1655677; abst. C. A. 1928, **22**, 1041; J. S. C. I. 1928, **47**, 295-B. E. P. 249946; abst. J. S. C. I. 1926, **45**, 532-B.

2. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 840326; abst. Textile Inst. J., 1931, **22**, 287-A. F. P. 654062. Cites E. P. 203092, 340324, 340325, 340436, 340437.

3. H. Dreyfus, F. P. Addn. 35947 to 634165; abst. C. A. 1930, **24**, 4171.

4. I. G. Farbenind. A.-G., Swiss P. 127261; abst. C. A. 1929, **23**, 1281. Belg. P. 352614, 354847.

5. W. Hentrich, U. S. P. 1695654; abst. J. S. C. I. 1929, **48**, 591-B.

L. Lilienfeld<sup>1</sup> has described the formation and application to the artificial filament industry, bookbinding and impregnation of textiles and for printing of the oxy- and hydroxy-alkylcelluloses, as 1,2-dihydroxypropylcellulose and hydroxy-ethylcellulose.

In the dyeing of materials made with cellulose derivatives as methyl-, ethyl- or benzyl-cellulose<sup>2</sup>, 1-*b*-hydroxyethylaminoanthraquinone sulfate or other suitable sulfuric ester of an anthraquinonylamine alcohol is used. Scarlet, violet, pure blue and bluish-red shades are obtained by the use of the sulfuric ester of 1-*b*-hydroxyethylamino-anthraquinone, -2-methylantraquinone, -4-hydroxyanthraquinone, -4-aminoanthraquinone, -2-brom-4-aminoanthraquinone, and -4-methylaminoanthraquinone. As plasticizing agents for methylcellulose and other cellulose ethers and esters<sup>3</sup>, methyl, propyl, *n*-butyl, and isobutyl glycolates and thioglycolates have been patented.

**Researches Published During 1929.** The year 1929 is especially conspicuous in the cellulose ether art by the number and relative importance of communications published and patents granted, as evidenced by the over two hundred and fifty separate contributions epitomized herein.

The Aceta<sup>4</sup> have found that the tensile strength of filaments of cellulose ethers and esters produced by the wet-spinning process may be augmented by the addition of a salt having a swelling action to the precipitating bath (thiocyanates or zinc chloride), or a colloid as molasses or sulfite-cellulose lye. A cellulose ether may be precipitated in a suitable form from its solution in a volatile solvent by means of a hydrocarbon boiling above 80° (toluene, xylene,

1. Aust. P. 111233. Australia P. 5422, 1927; 13743, 1928.
2. H. Olpin, U. S. P. 1688553; abst. C. A. 1929, **23**, 289; J. S. C. I. 1928, **47**, 926-B. E. P. 285641; abst. J. S. C. I. 1928, **47**, 364-B.
3. J. Payman and Imperial Chemical Industries, F. P. 662721; abst. Chem. Zentr. 1929, II, 2399. Australia P. 16635, 1928.
4. E. P. 310842; abst. C. A. 1930, **24**, 724; J. S. C. I. 1930, **49**, 943-B; Chem. Zentr. 1929, II, 2743; Silk. J. 1929, **6**, #63, 68. F. P. 672962; abst. C. A. 1930, **24**, 2293; Cellulose, 1930, **1**, 246. D. R. P. 513375; abst. C. A. 1931, **25**, 1380.

cyclohexane), or by benzonitrile or nitrobenzene<sup>1</sup>. Or<sup>2</sup>, by higher fatty acid ester of a monohydric alcohol, such as methyl-, ethyl-, propyl-, or amyl-stearate, -oleate or -palmitate. Certain halogenated compounds are also useful<sup>3</sup>, as di- or tri-chlorethylene, pentachlorethane, monochlorbenzene, monochlortoluene, *a*-bromnaphthalene, 1.2.3-trichlorbenzene, benzyl chloride, or by means of aromatic nitriles (benzo-, toluo- or xylo-nitriles).

E. Berl and H. Schupp<sup>4</sup> have given a detailed account of the methylation and ethylation of cellulose. Methylation of cellulose (linters) with 15% NaOH solution at ordinary temperatures affords first a monomethylcellulose, partly soluble in water, completely in Schweitzer's reagent and insoluble in the usual organic solvents. Further methylation produces ethers of gradually increasing methyl content, until trimethylcellulose results (25-28 methylations). Solubility in water of the methylated celluloses diminishes with increasing methoxyl content, finally becoming insoluble. Methylation of alkali-soluble cellulose gives ethers containing 19.17-30.71% MeO, according to the amount of methyl sulfate used.

Ethylation of cellulose with ethyl chloride and sodium hydroxide forms products having varying compositions and properties. Thus, at 100-120° under identical conditions the ethylated derivative is almost completely soluble in alcohol, while at 60-80°, the product is only partially so. Ethylation with 16 mols. ethyl chloride at 115° gives a product (2.5 ethoxyl groups per mol.) partly soluble in chloroform, dichlorethylene and benzene, insoluble in all other solvents. Further ethylation at 100° gives triethylcellulose, also obtained by direct ethylation at 115° with 48 mols. ethyl chlo-

1. H. Barthelemy, E. P. 308271; abst. C. A. 1930, **24**, 240; J. S. C. I. 1929, **48**, 513-B; Silk J. 1929, **6**, #62, 70. F. P. 638896; abst. C. A. 1929, **23**, 514. Cf. E. P. 282787.

2. H. Barthelemy, E. P. 308272; abst. J. S. C. I. 1929, **48**, 513-B; Silk J. 1929, **6**, #62, 70.

3. H. Barthelemy, E. P. 308273; abst. J. S. C. I. 1929, **48**, 513-B.

4. Cellulosechem. 1929, **10**, 41; abst. J. S. C. I. 1929, **48**, 278-B; C. A. 1929, **23**, 4816; Chem. Zentr. 1929, II, 3088.



ride giving a product soluble in chloroform, dichlorethylene, benzene and acetic acid.

Certain sulfo-fatty acid esters (isopropyl-, cetyl-, benzyl-, cyclohexanol- sulforicinoleates, -sulfoleates) when combined with alkylcelluloses<sup>1</sup>, constitute preparations capable of converting water-insoluble substances into perfect and permanent dispersions. In forming floor or wall coverings<sup>2</sup>, benzylcellulose is plasticized by gelatinizing agents as tolyl phosphate mixed with fillers or linoxyn, and applied to jute or other fabric. J. Bouchet<sup>3</sup> has published a process for the manufacture and purification of benzyl-cellulose, especially dibenzylcellulose, comprising treating alkalicellulose prepared with concentrated sodium hydroxide with benzyl chloride at 70-100° with or without a diluent. Methyl-, ethyl- or benzyl-cellulose is prepared by British Celanese, Ltd.<sup>4</sup>, by treating cellulosic material with an etherifying agent (ethyl sulfate) in the presence or absence of a small quantity of an alkaline material (sodium hydroxide or carbonate) for several hours at 0-45°, and afterwards with caustic soda in the solid form, the temperature being maintained at 30-60° until the cellulose ether is formed.

They obtain warp print effects by the local application of dyes to a fabric having a warp and a weft<sup>5</sup>, one of which consists of cellulose ether yarns, and the other of yarns of different dyeing properties, dispersed water-insoluble dyes being used to dye the cellulose ether portion, and have devised a method<sup>6</sup> comprising dyeing cellulose ether filaments while traveling, by the application of permanent coloring

1. H. T. Boehm, A. G., E. P. 313966; abst. C. A. 1930, **24**, 1247; Chem. Zentr. 1929, II, 2108. F. P. 679185, 679186; abst. C. A. 1930, **24**, 3911. F. P. 685994; abst. C. A. 1930, **24**, 6035. Cf. E. P. 306116.
2. H. Boernstein and N.-V. Nederlandsche Linoleumfabriek, E. P. 306140; abst. C. A. 1929, **23**, 5023; J. S. C. I. 1930, **49**, 420-B; Br. Plastics, 1930, **2**, #13, 53; Chem. Zentr. 1929, II, 112.
3. F. P. 693318; abst. C. A. 1931, **25**, 1671.
4. E. P. 315278; abst. C. A. 1930, **24**, 1740; J. S. C. I. 1930, **49**, 1022-B; Silk J. 1929, **6**, #66, 68; Br. Plastics, 1930, **2**, 322.
5. E. P. 316982; abst. C. A. 1930, **24**, 1991.
6. E. P. 313451, Addn. to E. P. 282036; abst. C. A. 1930, **24**, 1227; J. S. C. I. 1930, **49**, 1147-B; Chem. Zentr. 1929, II, 3253.

matters thereto in solutions of organic solvents. The process may be applied to the dyeing of similar threads while traveling<sup>1</sup>, or fabrics and products comprising a plurality of filaments, which are sprayed with a cellulose ether solution containing a polyglycol or its esters or ethers (mono-, di- or tri-methyl, ethyl, or propyl ethers of glycerol, ethyleneglycol or diethyleneglycol).

A resinous compound suitable for use in coating and plastic compositions containing cellulose ethers and esters<sup>2</sup>, is formed by heating lactic acid under a reflux condenser and then distilling off the volatile portion. In order to increase the solubility of the cellulose ethers<sup>3</sup>, the cellulose prior to etherification is treated with hydrofluoric acid. They tint cellulose ether fibers and filaments with fugitive tinting fluids for purposes of identifying them as to denier, count, twist or size<sup>4</sup>.

In order to obtain cellulose ether products which readily may be wetted<sup>5</sup>, there is added to the spinning solution of the ether, a relatively non-volatile substance which is water-soluble (ethylene glycol, diethylene glycol, glycerol, diacetone alcohol, monoacetin, ethyleneglycol monomethyl ether). In order to facilitate solution of the cellulose ethers<sup>6</sup>, they are first subjected to a solvent in the vapor phase, then with a liquid solvent in the usual manner.

1. E. P. 313450, Addn. to E. P. 282036; abst. C. A. 1930, **24**, 1227; J. S. C. I. 1930, **49**, 1147-B. See E. P. 314208.

2. British Celanese, Ltd., E. P. 311657; abst. C. A. 1930, **24**, 981; J. S. C. I. 1930, **49**, 1039-B.

3. *Ibid.* E. P. 308348; abst. C. A. 1930, **24**, 239; J. S. C. I. 1930, **49**, 610-B; Chem. Zentr. 1929, II, 813.

4. *Ibid.* E. P. 308733; Addn. to E. P. 282036, 308173; abst. C. A. 1930, **24**, 510; J. S. C. I. 1930, **49**, 1063-B; Silk J. 1929, **6**, #62, 72; Chem. Zentr. 1929, II, 657.

5. *Ibid.* E. P. 313885; abst. C. A. 1930, **24**, 1218; J. S. C. I. 1930, **49**, 1146-B; Silk J. 1929, **6**, #65, 78. In E. P. 316521, C. Dreyfus and G. Schneider saponify yarns and fabrics made of cellulose acetate, propionate or butyrate with caustic soda in paste form, using as a thickener the cellulose ethers because they are unaffected by the alkali, materials treated in this manner possessing higher safe ironing properties.

6. *Ibid.* E. P. 303152; abst. C. A. 1929, **23**, 4542; J. S. C. I. 1930, **49**, 828-B; Chem. Zentr. 1929, I, 2370.

In the treatment of fabrics made of or containing cellulose ethers and esters<sup>1</sup>, there is applied in a design a substance as gelatin or casein to prevent subsequent coloration, and thereupon dyeing the cellulose acetate derivative. In the weighing of cellulose ether fabrics by means of tin chloride fixed by sodium phosphate, sodium silicate or tannin<sup>2</sup>, to obtain an increased absorption of weighting material<sup>3</sup>, the product is treated simultaneously with a zinc salt as zinc chloride. In the production of cellulose ether plastics<sup>4</sup>, artificial resins formed by the condensation of xylene sulfonamide with an aldehyde (formaldehyde, paraformaldehyde, acetaldehyde) are mixed with methyl-, ethyl- or benzyl-cellulose in the presence of ethyl lactate and diethyl phthalate. Similar products result<sup>5</sup> by the substitution of benzene sulfonamide for the xylene compound, diphenylol propane and thiocarbanalide being plasticizing bodies recommended for use therewith.

Plastic bodies of a wide variety of uses are claimed to result when the cellulose ethers are incorporated with certain bromine substituted bodies, as the dibromides of cinnamic acid, styrol, cinnamyl alcohol and of cinnamaldehyde<sup>6</sup>, with a corresponding augmenting of the fire resistance. The halogenated derivatives of phenolic esters of the phosphoric acids<sup>7</sup> are also advocated as fulfilling the combined function of plasticizing and inflammability reducing, such as monobromphenyl-diphenyl, dibromphenyl-phenyl

1. British Celanese, Ltd., E. P. 316983, Addn. to E. P. 295582; abst. C. A. 1930, **24**, 1991; J. S. C. I. 1930, **49**, 506-B. In this connection see E. P. 182830, 194840, 219349, 224925, 295582, 314208.

2. E. P. 258874; abst. C. A. 1927, **21**, 3135.

3. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 309876, Addn. to E. P. 258874; abst. C. A. 1930, **24**, 735; J. S. C. I. 1929, **48**, 596-B; Silk J. 1929, **6**, #63, 66; Chem. Zentr. 1929, II, 1102.

4. British Celanese, Ltd., E. P. 315808; abst. C. A. 1930, **24**, 1754.

5. *Ibid.* E. P. 315807, 315808; abst. C. A. 1930, **24**, 1754.

6. *Ibid.* E. P. 313535; Addn. to E. P. 313134; abst. C. A. 1930, **24**, 1216; J. S. C. I. 1930, **49**, 1147-B; Br. Plastics, 1931, **2**, #20, 376.

7. *Ibid.* E. P. 313405; abst. C. A. 1930, **24**, 1216; J. S. C. I. 1930, **49**, 858-B; Br. Plastics, 1930, **2**, #17, 230.

and tribromophenyl phosphates. Or<sup>1</sup>, the bromine may be substituted in a halogen-substituted side chain, e.g., benzyl bromide, benzal bromide or benzotribromide.

As plasticizing bodies for such aralkylcelluloses as benzylcellulose<sup>2</sup>, certain synthetic resins as the cumarone series, the phthalic anhydride-glycerol resins and the polymerized lactic acid resins are advocated<sup>3</sup>. Other suitable plasticizing bodies which have received patent protection<sup>4</sup>, are the methyl, ethyl and phenyl esters of benzenesulfonic acid, and *o*- and *p*-toluenesulfonic acid. The cellulose ethers are rendered less flammable by incorporating with them aliphatic acyl derivatives of nuclear-chlorinated arylamines of the benzene series<sup>5</sup>, as acetylchloraniline (*o*-chloracetanilid), propionylchloraniline and butyrylchloraniline. Acidylated amino-phenols have also been patented as cellulose ether plasticizing bodies<sup>6</sup>, e.g., acetyl-, propionyl- or butyryl-anisidine or -phenetidine, propyloxy-acetanilid and butyloxy-acetanilid. Likewise for the same purpose, acidyl derivatives of halogenated amines, e.g., acetylmonochloraniline, butyrylmonobromaniline or propionyl-*o*-chloraniline, with various other modifying ingredients.

Coating compositions have been described containing methyl-, ethyl- and benzyl-cellulose<sup>7</sup> of low viscosity characteristics, combined with synthetic resins of the diphenylol-aldehyde, diphenylol-propane-ketone and acetone-furfural types, alone or in conjunction with such natural resins

1. British Celanese, Ltd., E. P. 313134; abst. C. A. 1930, **24**, 961; J. S. C. I. 1930, **49**, 1061-B.

2. H. Dreyfus, E. P. 164375; abst. C. A. 1922, **16**, 493; J. S. C. I. 1921, **40**, 540-A.

3. British Celanese, Ltd., E. P. 313133; abst. C. A. 1930, **24**, 960; J. S. C. I. 1930, **49**, 726-B; Br. Plastics, 1930, **2**, #17, 100. See G. Schneider, E. P. 309913; abst. C. A. 1930, **24**, 723.

4. *Ibid.* E. P. 312688; abst. C. A. 1930, **24**, 960; Silk J. 1929, **6**, #64, 68; J. S. C. I. 1930, **49**, 985-B.

5. *Ibid.* E. P. 312609; abst. C. A. 1930, **24**, 960; J. S. C. I. 1930, **49**, 1023-B; Br. Plastics, 1930, **2**, #19, 322.

6. *Ibid.* E. P. 312606; abst. C. A. 1930, **24**, 960; J. S. C. I. 1930, **49**, 943-B; Silk J. 1929, **6**, #64, 68; Br. Plastics, 1930, **2**, 278.

7. *Ibid.* E. P. 309951; abst. C. A. 1930, **24**, 739; Chem. Zentr. 1929, II, 1364.

as manilla, acaroid, pontianak, kauri, dammar, copal, rosin (colophony) or shellac.

Compositions useful in the production of cellulose ether silks result by combining the ether<sup>1</sup> with an arylsulfonanilid or alkyl derivative thereof, examples being benzene- and *o*-toluene-sulfonanilid and their N-methyl derivatives; the N-ethyl toluene-*p*-sulfonanilid, "dibenzene sulfonanilid" and toluene disulfonanilid. Compositions especially applicable to uniting sheets of glass are obtainable by combining methyl- or benzyl-cellulose with diphenylol propane in the presence of 1-6% of water<sup>2</sup>. Protective coatings for such materials as toilet articles, fountain pens, blocks and sheets<sup>3</sup> are formed by coating first with a cellulose ether in solution, then with an artificial resin also in the dissolved state. In the production of discharge effects on materials made of or containing cellulose ethers<sup>4</sup>, hydrogen peroxide, silver peroxide, nitric acid, acid permanganate or sodium peroxide are recommended, and especially<sup>5</sup> bleaching powder followed by citric acid as being preferable to a potassium chlorate treatment.

Pattern effects may be produced upon textile materials of cellulose ethers<sup>6</sup> by oxidation, after application thereto of an amine capable of yielding a coloration on oxidation, then applying locally an agent inhibiting the formation of the coloration. To produce mat effects upon cellulose ether textiles<sup>7</sup>, they are treated with an "effect composition" containing a water-insoluble thickening material such as nitro-

1. British Celanese, Ltd., E. P. 308798; abst. C. A. 1930, **24**, 498; Chem. Zentr. 1929, II, 1104.

2. *Ibid.* E. P. 317443; abst. C. A. 1930, **24**, 2292.

3. *Ibid.* E. P. 316984; abst. C. A. 1930, **24**, 1996. See also E. P. 299065, 299066, 299067, 307290, 307291.

4. *Ibid.* E. P. 315005; abst. C. A. 1930, **24**, 1522; J. S. C. I. 1931, **50**, 292-B.

5. British Celanese, Ltd., and G. Ellis, E. P. 312655; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 678-B.

6. H. Platt and C. Dreyfus, E. P. 314501; abst. C. A. 1930, **24**, 1523; Silk J. 1929, **6**, #66, 68. C. Dreyfus, F. P. 676830; abst. C. A. 1930, **24**, 3119.

7. British Celanese, Ltd., E. P. 314396; Addn. to E. P. 274841; abst. C. A. 1930, **24**, 1524; J. S. C. I. 1930, **49**, 1106-B.

cellulose or ethylcellulose, an "effect material" as a pigment, and a solvent for the thickening agent which is not a solvent for the fabric being treated.

To improve the hot-ironing properties of cellulose ether and ester materials<sup>1</sup>, they are dyed with logwood black which raises the fusing point of the cellulose derivative by 20° or more. In the production of fabrics having luster effects, two types of cellulose derivatives (acetate and ethylcellulose) are woven together, one type being easily de-lustered by boiling water or soap solutions, and the other being more resistant, then subjecting the fabric to a de-lustering process such as immersion in a boiling soap bath<sup>2</sup>. It has been proposed<sup>3</sup> to use methyl-, ethyl- or benzyl-cellulose in fibrous form for heat and sound insulation.

In the W. Moss and B. White method for producing coating compositions containing cellulose ethers<sup>4</sup>, the ether and a resin of the toluenesulfonamide type are plasticized by the addition of such substances as triacetin, diphenylol propane or monomethylxylenesulfonamide. To augment the tensile strength of cellulose ethers<sup>5</sup>, especially in the filament and film form, various synthetic resins are added in 1-25% of the quantity of cellulose ether used. In reducing the luster of artificial filaments prepared from cellulose ethers<sup>6</sup>, insoluble (especially white) salts are precipitated in the material, preferably in the presence of swelling agents (which may also serve as one of the reacting components to form the precipitate); e.g., barium sulfocyanide and sulfuric acid, or phosphoric acid.

1. British Celanese, Ltd., E. P. 313970; abst. C. A. 1930, **24**, 1227; J. S. C. I. 1930, **49**, 1025-B; Chem. Zentr. 1929, II, 2941. See E. P. 263222.

2. *Ibid.* E. P. 310845; abst. C. A. 1930, **24**, 734; J. S. C. I. 1930, **49**, 858-B; Chem. Zentr. 1929, II, 2507. Cf. E. P. 320363.

3. *Ibid.* E. P. 315280; abst. C. A. 1930, **24**, 1685.

4. E. P. 317454; abst. C. A. 1930, **24**, 2292.

5. British Celanese, Ltd., E. P. 317457; abst. C. A. 1930, **24**, 2291.

6. *Ibid.* E. P. 318467; abst. C. A. 1930, **24**, 2311.

In producing hollow artificial silk and horsehair<sup>1</sup>, a cellulose ether in solution is extruded into a precipitating bath or into an evaporative atmosphere under conditions which first effect a slow solidification, followed by a more rapid solidification. In another method for hollow filament formation of artificial silk from cellulose ethers<sup>2</sup>, a slow spinning rate is employed (about 0.025-0.15 m. per min.), the size of the extrusion orifice varying inversely with the denier of the filament, while the rate of spinning varies inversely with the weight of the filaments. The latter after spinning, are preferably drawn out.

In order to increase the solubility of cellulose ethers, the cellulose before etherification is preliminarily treated with nitric acid, or, methyl-, ethyl- or benzyl-cellulose may be treated with nitric acid after formation. The nitric acid varies in strength from 5-70%. With the latter strength, mixed ether-esters are formed, such as methylcellulose nitrate, ethylcellulose nitrate, benzylcellulose nitrate<sup>3</sup>. Thermoplastic powders comprising an intimate mixture of cellulose ether with plastifiers<sup>4</sup>, are molded under heat and pressure, and may be rendered incombustible by incorporating ammonium bromide or phosphate. In the formation of coated articles<sup>5</sup>, fine powdered cellulose ethers are ground with solid plasticizers which are then sprinkled upon the article to be coated and made to coalesce by combined heat and pressure.

1. British Celanese, Ltd., E. P. 318629; abst. C. A. 1930, **24**, 2294; Rayon Record, 1930, **4**, #2, 99.

2. *Ibid.* E. P. 318632; abst. C. A. 1930, **24**, 2294; Silk J. 1929, **6**, #67, 72.

3. *Ibid.* E. P. 319691; abst. C. A. 1930, **24**, 2599; Cellulose, 1930, **1**, 150; Silk J. and Rayon World, 1930, **6**, 68. See C. Dreyfus, E. P. 308322, 308587.

4. *Ibid.* E. P. 303516; Addn. to E. P. 282723; abst. C. A. 1929, **23**, 4571; J. S. C. I. 1930, **49**, 553-B; Chem. Zentr. 1929, I, 2371.

5. *Ibid.* E. P. 303898; abst. C. A. 1929, **23**, 4582; J. S. C. I. 1930, **49**, 571-B; Chem. Zentr. 1929, I, 2590. See W. Moss, E. P. 298608; abst. C. A. 1929, **23**, 3098.

In the formation of composite sheets pervious to ultra-violet rays<sup>1</sup>, sheets of material such as pure quartz glass are united with an intermediate layer of cellulose ether or ester under the action of heat and pressure. To produce celluloid substitutes<sup>2</sup>, synthetic resin produced from acetone and furfural are added to methyl-, ethyl- or benzyl-cellulose lacquers, and a volatile solvent as ethyl acetate or lactate, tetrachlorethane or benzyl alcohol used as a diluent. Aniline-furfural synthetic resins<sup>3</sup> are also applicable, as are those artificial resins formed by the condensation of furfuraldehyde with an aromatic amine (aniline)<sup>4</sup>. Instead of a synthetic resin<sup>5</sup>, natural resins as manila, aca-roid, pontianak, kauri, dammar or an ester gum (glyceryl ester of rosin) may be used with the cellulose ether, high boilers and ancillary solvents being incorporated to give the flowability desired.

A surgical dressing or catamenial pad has been described<sup>6</sup>, having a surface adapted to contact with the body and made of a fabric containing a cellulose ether and an intermediary layer of more absorbent material.

In the temporary coloration of textile filaments and yarns containing cellulose ethers<sup>7</sup>, solutions of dyestuffs in liquids of boiling points above 100° are employed, examples of such liquids found suitable being ethylene glycol (b. pt. 197.5°), diethylene glycol (250°), ethyleneglycol monoethyl ether (135.5°), and diethyleneglycol monoethyl ether

1. British Celanese, Ltd., E. P. 306397; abst. C. A. 1929, **23**, 502; J. S. C. I. 1930, **49**, 714-B; Chem. Zentr. 1929, I, 3131.

2. *Ibid.* E. P. 307289; abst. J. S. C. I. 1930, **49**, 469-B; Chem. Zentr. 1929, I, 3152.

3. *Ibid.* E. P. 307290; abst. C. A. 1929, **23**, 5338; J. S. C. I. 1930, **49**, 469-B; Chem. Zentr. 1929, I, 3152; Br. Plastics, 1930, **2**, #13, 53 (suppl.).

4. British Celanese, Ltd., E. P. 307291; abst. C. A. 1929, **23**, 5338; British Plastics, 1930, **2**, #13, 53 (suppl.); Chem. Zentr. 1929, I, 3152.

5. *Ibid.* E. P. 307292; abst. C. A. 1929, **23**, 5338; Chem. Zentr. 1929, I, 3152.

6. *Ibid.* E. P. 307459; abst. C. A. 1929, **23**, 5276; J. S. C. I. 1930, **49**, 441-B. Can. P. 315580.

7. *Ibid.* E. P. 308173; abst. C. A. 1930, **24**, 247; J. S. C. I. 1930, **49**, 1062-B; Silk J. 1929, **6**, #62, 70; Chem. Zentr. 1929, II, 657.



(187.5°). The inflammability of the cellulose ethers may be lessened by the addition of a bromine derivative of an acetylated aromatic amine (acetyl-4-bromomethylanilid, acetyl-2-4- or -3,4-dibromanilid, acetyl-2,4,6- or -2,4,5-tribromanilid, acetyl-2,4,6-tribromomethylanilid, diacetyl-3,5-dibrom-2-toluidid, diacetyl-1,3,6-tribrom-2-naphthalid or benzoyl-2,4,6-tribromanilid<sup>1</sup>.

In a process for cutting, dividing, parting, trimming and perforating cellulose ether fabrics<sup>2</sup>, the fabric is first treated with a solvent or softener of the ether which is afterwards cut with a hot knife or wire, the hot cutting iron softening and sealing the edges so that a lower cutting temperature may be used and the cut edges effectively sealed against fraying and ravelling. Cellulose ether silk may be dyed with unsulfonated nitroarylated carbamides or thiocarbamides, or with unsulfonated aminoarylated carbamides or thiocarbamides, diazotized and coupled on the fiber with developed components, examples being 2,4-dinitrophenyl-carbamide (yellow), 4,4'-diaminodiphenylcarbamide + 2 mols. phenol (yellow), or *m*-phenylenediamine (golden-orange)<sup>3</sup>. Or the silk may be dyed in reddish or greenish-blue shades with azo dyes made by coupling a diazotized aminoxanthen, as Rhodamine 3G extra (Color Index No. 753) with suitable components as phenol, *m*-toluidine or dimethylaniline<sup>4</sup>. In the production of black colorations<sup>5</sup> on mixed materials containing cellulose ethers or esters, acetate filaments, cotton, viscose silk or wool materials are

1. British Celanese, Ltd., and A. Daly, E. P. 319073; abst. C. A. 1930, **24**, 2599; J. S. C. I. 1930, **49**, 53-B; Brit. Plastics, 1930, **1**, #10, 447.

2. British Celanese, Ltd., and W. Dickie, E. P. 305257; abst. J. S. C. I. 1929, **48**, 279-B; Silk J. 1929, **5**, #60, 66; Chem. Zentr. 1929, II, 512. See E. P. 299042.

3. British Celanese, Ltd., H. Dreyfus, G. Ellis, T. Ockman and H. Olpin, E. P. 316526; Addn. to E. P. 291118; abst. C. A. 1930, **24**, 1991; J. S. C. I. 1929, **48**, 894-B. Cites E. P. 283253. D. R. P. 268658.

4. British Celanese, Ltd., and G. Ellis, E. P. 311433; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 678-B; Chem. Zentr. 1929, II, 2506. See E. P. 219349, 224925, 242393, 242711, 269960, 273819, 273820.

5. *Ibid.* E. P. 311435; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 678-B; Chem. Zentr. 1929, II, 2506.

dyed in level shades by applying a mixture of *p*-aminodiphenylamine and aniline, equal parts, followed by oxidation in the usual manner.

In order to secure level dyeing of ester and ether filaments<sup>1</sup> in the form of cops, pirns, cheeses and rolls, an insoluble dye is applied in colloidal suspension. In the dyeing of cellulose ethers<sup>2</sup>, unsulfonated thiazole derivatives are used<sup>3</sup>, examples being compounds obtained by diazotizing or condensing dehydrothio-*p*-toluidine with phenol (yellow shade), *m*-toluylenediamine (yellow), 2,4-dinitrochlorobenzene (yellow), *m*-toluidine (yellow), or 2,5-dichlorobenzene (yellow). It has been found that the combined mordanting and weighting of cellulose ether filaments<sup>4</sup> may be effected at lower temperatures if zinc chloride is used. Materials containing cellulose ethers are dyed by means of aqueous dispersions of amino-, alkylamino- or aralkylamino-substituted derivatives (in their unreduced state) of benzo- or naphtho-quinones or substitutents, e.g., 2,5-diaminobenzoquinone dispersed by means of Turkey red oil gives a yellow color<sup>5</sup>.

Cellulose esters and ethers are tinted<sup>6</sup> by using in the unreduced state N-arylated nitrogen-containing derivatives of benzo- and naphtho-quinones (indophenols excepted), examples being, 2,5-di(phenylamino)benzoquinone (reddish-grey), 2,5-di(phenylamino)benzoquinone (brown), 2,5-di(*p*-dimethylamino-phenylamino)-benzoquinone (purplish-

1. British Celanese, Ltd., G. Ellis and T. Ellison, E. P. 311675; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 678-B; Chem. Zentr. 1929, II, 2506. See also E. P. 220505, 224681, 227183, 237943, 239470, 253978, 263260, 283081, 283253, 299343, 300929, 305560, 306981, 310827.

2. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 306981; abst. C. A. 1929, **23**, 5330; J. S. C. I. 1929, **48**, 354-B; Chem. Zentr. 1929, II, 99.

3. Other than basic dyes described as used with cellulose ethers in E. P. 196953; abst. C. A. 1924, **17**, 3794.

4. *Ibid.* E. P. 309899; abst. C. A. 1930, **24**, 733; J. S. C. I. 1929, **48**, 596-B; Silk J. 1929, **6**, #63, 66; Chem. Zentr. 1929, II, 1102.

5. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 321401; abst. C. A. 1930, **24**, 2897; J. S. C. I. 1930, **49**, 54-B.

6. *Ibid.* E. P. 322463; abst. C. A. 1930, **24**, 2897; J. S. C. I. 1930, **49**, 320-B.

brown), 2-*p*-anisidino-1.4-naphthoquinone (dull scarlet), 2-(*p*-aminophenylamino)-1.4-naphthoquinone (heliotrope), 1-imino-2-hydroxy-4-*p*-tolyliminonaphthalene (orange), and 1-imino-2-hydroxy-4-(4'-aminophenylimino)naphthalene (puce).

In the preparation of wetting and dispersing agents which are suitable for use in dyeing cellulose ethers and esters<sup>1</sup>, furfural or its derivatives such as methylfurfural or furfuramide are condensed with naphthalene, anthracene, or carbazole, and the products in solution used in conjunction with the cellulose compounds. Ether filaments may be colored with azo dyes obtained by diazotizing or tetrazotizing a mono- or di-aminoanthraquinone and coupling, examples being 1-aminoanthraquinone with *m*-toluidine (yellow), or with anthranilic acid (golden orange), and 1-amino-2-methylantraquinone with dimethyl-*m*-aminophenol (orange)<sup>2</sup>. In another method<sup>3</sup> a dispersion of a free hydroxynaphthoic acid arylide is applied to the material and developed with a diazo compound.

In dyeing with diazotized and coupled 3.5-dinitro-*o*-toluidines, -*o*-anisidines or -*o*-phenetidines<sup>4</sup>, the dyes may be produced on the fiber by padding with  $\alpha$ -naphthylamine and developing with the diazotized amine.

Artificial silks exhibiting a reduced luster or even a dull mat appearance<sup>5</sup>, result by the dry-spinning of solutions of the cellulose ethers in volatile solvents, the filaments being extruded into an atmosphere containing one

1. British Celanese, Ltd., G. Ellis, H. Olpin and E. Kirk, E. P. 322737; abst. C. A. 1930, **24**, 2900; J. S. C. I. 1930, **49**, 361-B.

2. British Celanese, Ltd., G. Ellis, H. Olpin and D. Mosby, E. P. 310827; abst. C. A. 1930, **24**, 733; J. S. C. I. 1929, **48**, 678-B; Chem. Zentr. 1929, II, 2376.

3. British Celanese, Ltd., G. Ellis, H. Olpin and E. Walker, E. P. 310779; abst. C. A. 1930, **24**, 733; J. S. C. I. 1929, **48**, 678-B; Chem. Zentr. 1929, II, 2506.

4. British Celanese, Ltd., D. Mosby, H. Olpin and G. Ellis, E. P. 319390; abst. C. A. 1930, **24**, 2615; J. S. C. I. 1930, **49**, 139-B. See E. P. 319308.

5. British Celanese, Ltd., R. Payne and R. Roberts, E. P. 314404; abst. C. A. 1930, **24**, 1509; J. S. C. I. 1929, **48**, 714-B; Silk J. 1929, **6**, #65, 80.

or more organic precipitants, the spinning conditions being so adjusted that they exert a precipitating action on the cellulose ether during the early stages of filament formation. As precipitants<sup>1</sup> alcohols, hydrocarbons and esters are claimed as suitable. R. Brownlow<sup>2</sup> says that cellulose ether products of improved clarity may be produced, suitable for conversion into cinematograph films or transparent foil for wrapping foodstuffs, if, in the preparation of a solution of the cellulose derivatives, phosphorus oxychloride or sulfur oxychloride in association with metal halidies (zinc chloride) is added, quantities up to 5% (on the weight of cellulose derivatives) of a 2:1 mixture of sulfur oxychloride and zinc chloride being cited.

J. Capstaff<sup>3</sup> claims that halation in plates or films for lenticular-screen or multicolor-screen photography is avoided by including in the support a light-absorbing dye, the dye being mixed with the film base dope which may include a cellulose ether. C. Carroll<sup>4</sup> prepares cellulose ether films of low inflammability by incorporating therein bromine substituted derivatives of catechol, resorcinol, hydroquinone, pyrogallol, cresol or thymol, tribromphenol with water-insoluble ethylcellulose being especially useful. Bromcamphor<sup>5</sup> has been patented for the same purpose, as has<sup>6</sup> brom-benzene, -toluene, -xylene, -mesitylene, -ethylbenzene, -cumene, and -cymene, including mono-, di- and tri-brom derivatives. A cellulose ether composition of low evaporative tendency has been described in which the solvent used

1. British Celanese, Ltd., E. P. 314414; abst. J. S. C. I. 1929, **48**, 714-B; Silk J. 1929, **6**, #65, 80.

2. E. P. 322464; abst. C. A. 1930, **24**, 2881; J. S. C. I. 1930, **49**, 184-B; Brit. Plastics, 1930, **1**, #10, 447.

3. E. P. 312992; abst. J. S. C. I. 1930, **49**, 841-B. Compare U. S. P. 1374871.

4. U. S. P. 1716418; abst. C. A. 1929, **23**, 3807; J. S. C. I. 1930, **49**, 413-B; Plastics, 1930, **6**, #1, 26.

5. S. Carroll, U. S. P. 1716419; abst. C. A. 1929, **23**, 3807; J. S. C. I. 1930, **49**, 413-B; Plastics, 1930, **6**, #1, 26.

6. *Ibid.* U. S. P. 1716420; abst. C. A. 1929, **23**, 3807; J. S. C. I. 1930, **49**, 413-B; Plastics, 1930, **6**, #1, 26.

is ethyleneglycol diacetate<sup>1</sup>. He has also patented the use of monoalkyl (methyl, ethyl, propyl, butyl, amyl) ethers of ethylene glycol (which are non-solvents of cellulose ethers)<sup>2</sup> with the alkylcelluloses in conjunction with volatile solvents to induce suppleness and flexibility, especially applicable to film formation. Ethylene glycol also falls in this category<sup>3</sup>.

Whereas the vinyl esters merely gel ethyl- and benzyl-cellulose or only dissolve them slowly, it has been found<sup>4</sup> in the presence of a suitable auxiliary substance as alcohol, valuable solvent combinations result. The vinyl compounds described as most useful in connection with the cellulose ethers are the acetate, propionate, phthalate, phosphate, chloride, bromide, or styrene (vinyl benzene), yielding celluloids of high tensile strength. Or polymerized vinyl compounds of the above may be used<sup>5</sup>. It is claimed that films and sheets of methyl- or ethyl-cellulose may best be prepared<sup>6</sup> from solutions or dopes by extruding or causing them to flow at elevated temperatures, thereby enabling less solvent to be employed, which results in more rapid setting and drying and consequently in an increased rate of production.

Sheet material for wall purposes<sup>7</sup> is formed by embedding an open-work, reticulated or tessellated reinforcement such as metallic wire netting in a composition comprising a cellulose ether with fillers. Or a sheet or film may be prepared by spreading a solution of a cellulose ether

1. British Celanese, Ltd., U. S. P. 1735156; abst. C. A. 1930, **24**, 723; Cellulose, 1930, **1**, #7, 35.

2. *Ibid.* U. S. P. 1735157; abst. C. A. 1930, **24**, 723.

3. *Ibid.* U. S. P. 1735158; abst. C. A. 1930, **24**, 723; Cellulose, 1930, **1**, #2, 63.

4. Celluloid Corp., E. P. 308657; abst. C. A. 1930, **24**, 499; J. S. C. I. 1930, **49**, 943-B; Brit. Plastics, 1930, **2**, #18, 278; Kunst. 1931, **21**, 16; Chem. Zentr. 1929, II, 814.

5. *Ibid.* E. P. 308658; abst. C. A. 1930, **24**, 499; J. S. C. I. 1930, **49**, 1146-B; Chem. Zentr. 1929, II, 814.

6. Celluloid Corp., E. P. 310540; abst. C. A. 1930, **24**, 723; J. S. C. I. 1930, **49**, 943-B.

7. *Ibid.* E. P. 310541; abst. C. A. 1930, **24**, 723.

or ester<sup>1</sup> onto the surface of a moving, inert medium as mercury, or a low-melting alloy, evaporating the solvent from the deposited solution, and stripping the sheet from the surface of the liquid.

In the J. Chamberlain and H. Periam photographic film<sup>2</sup>, a substratum of ethylcellulose composition is used between the celluloid support and the lightsensitive layer, and this substratum may carry coloring substances, or a multicolor dot screen for photography, the cellulose ether being dissolved in benzene. In the production of white or colored discharges upon materials made of or containing cellulose ethers<sup>3</sup>, the operation may be facilitated by preliminary treatment of the materials with metallic salts capable of forming compounds with the dyes, such as salts of tin, aluminum, zinc, iron or chromium, which are preferably applied in the form of printing pastes in the presence of acids or acid salts, after which the materials are dyed and subjected to discharge printing.

L. Clement and C. Riviere<sup>4</sup> report that benzylcellulose may readily be obtained by acting with benzyl chloride at definite temperatures upon alkalicellulose, the benzyl ether formed being soluble in acetone, in a mixture of alcohol and benzene, and in cyclohexanone and cyclohexanol, and point out the possible uses in the arts of benzylated cellulose. In the production of artificial leather from the cellulose ethers<sup>5</sup>, the basic fibrous material or the tips of its fibers are superficially impregnated with a thin layer of cellulose ether or ester or with a solvent for the same, the cellulose

1. British Celanese, Ltd., E. P. 315840; abst. C. A. 1930, **24**, 1740.

2. E. P. 304632; abst. C. A. 1929, **23**, 4630; J. S. C. I. 1929, **48**, 265-B; Chem. Zentr. 1929, II, 2630.

3. R. Clavel, E. P. 308757; abst. C. A. 1930, **24**, 510; J. S. C. I. 1930, **49**, 238-B; Silk J. 1929, **6**, #62, 72; Chem. Zentr. 1929, II, 656. F. P. 657003; abst. C. A. 1929, **23**, 4350. See E. P. 270987, 277602, 280094, 300894, 303129.

4. Chim. et Ind. 1928, April, Special No., 670; abst. C. A. 1928, **22**, 3293; I. E. C. (News Ed.) 1928, Jan. 10, 6; Z. Angew. Chem. 1927, **40**, 1579; Chem. Zentr. 1929, I, 955.

5. Compagnie Francaise d'Exploitation des Procédés Plinatus, E. P. 317824; Addn. to E. P. 301759; abst. J. S. C. I. 1930, **49**, 985-B; Brit. Plastics, 1930, **2**, #18, 279.

mass being subsequently applied before all of the solvent has evaporated.

E. Desparmet<sup>1</sup> prepares butylcellulose (?) by the action of butyl chloride upon cellulose in the presence of pyridine, diethylaniline or dimethylaniline, and cellulose butyrate by the action of butyric anhydride upon cellulose in the presence of a catalyst. Wool fabrics are cleansed and prepared for dyeing<sup>2</sup> by treatment with cellulose ether solvents, especially methylethyl ketone and chlorinated hydrocarbons (isopropyl chloride). A method has been devised for protecting the exposed surface of percussion caps<sup>3</sup> from moisture and damage during insertion into the cartridge, by coating the same with esters, ethers or mixed ester-ethers of cellulose. In the printing of fabrics or fibers of cellulose ethers or esters<sup>4</sup>, where vat dyes are used which produce delustering of the silk, an addition of one or more of the following agents is made to the printing paste to prevent or inhibit the loss of luster: methyl and ethyl ethers of ethylene glycol with or without alcohol, benzyl alcohol, triacetin, cyclohexanone, potassium or ammonium thiocyanate, sugar, phthalimide and xylyl monomethylsulfonamide.

An excellent cellulose ether or ester lacquer formula<sup>5</sup> is said to result upon mixing ethyl alcohol 30, benzene 40, and ethylene dichloride 30. C. Dreyfus<sup>6</sup> has published a process for ethylating cellulose which comprises pretreating the cellulose with ethyl alcohol and an alkali and subsequently treating the cellulose with a mixture of phosphoric acid and ethyl alcohol. A phonograph sound record has

1. F. P. 664932; abst. C. A. 1930, **24**, 961.

2. Deutsche Wollenwaren Manufaktur, A. G., E. P. 308605; abst. C. A. 1930, **24**, 511; J. S. C. I. 1930, **49**, 859-B; Chem. Zentr. 1929, II, 656.

3. W. Dickson and Imperial Chemical Industries, Ltd., E. P. 307560; abst. C. A. 1929, **23**, 5319; J. S. C. I. 1929, **48**, 418-B. F. P. 671683; abst. C. A. 1930, **24**, 2297.

4. C. Dreyfus, E. P. 306534; abst. C. A. 1929, **23**, 5048; J. S. C. I. 1930, **49**, 702-B; Silk J. 1929, **6**, #61, 72; Chem. Zentr. 1929, II, 221. Cf. E. P. 246879; abst. J. S. C. I. 1926, **45**, 317-B. E. P. 259266; abst. J. S. C. I. 1926, **45**, 977-B.

b. *Ibid.* Can. P. 293642.

6. Can. P. 286918.

been described<sup>1</sup> in which at least the portion which contains the sound record track is composed of a cellulose ether and a plastifier.

Cellulose ether filaments are producable by the dry-spinning method<sup>2</sup>, in which the dissolving portion comprises a volatile solvent (acetaldehyde, methyl or ethyl formate, acetone) together with a non-solvent of higher boiling point than the solvent portion (benzene, xylene, propyl alcohol), the idea being that upon evaporation first of the solvent, precipitation of filament will ensue due to increasing amount of non-solvent left behind. For the manufacture of films<sup>3</sup>, cellulose ethers are dissolved in an aqueous or organic solution of urea, thiourea, guanidine, dimethylurea, diethylurea or similar ureoid base, with or without the aid of plasticizers.

Patterns may be produced upon materials containing cellulose ethers or esters<sup>4</sup>; by locally applying a composition containing a chlorate and then one or more colors dischargeable thereby. Glycollic acid may be produced catalytically from oxalic acid in the presence of nickel<sup>5</sup>; while dimethyl ether may be converted into methoxyacetic acid, and diethyl ether into *b*-ethoxypropionic acid, by passing it with excess of carbon dioxide at 100-200 atm. over phosphoric acid on coke as catalyst. The anhydride of methoxyacetic acid<sup>6</sup> is prepared by causing an alkali salt of the same to react with sulfur chloride, sulfonyl chloride or

1. C. Dreyfus, Can. P. 288362.

2. H. Dreyfus, E. P. 312203; abst. C. A. 1930, **24**, 963; J. S. C. I. 1929, **48**, 594-B; Silk J. 1929, **6**, #64, 66. F. P. 666897; Addn. 38124 thereto.

3. *Ibid.* E. P. 315766; abst. C. A. 1930, **24**, 1740; J. S. C. I. 1930, **49**, 1147-B; Brit. Plastics, 1931, **2**, #20, 146; Cellulose, 1930, #5, 150.

4. *Ibid.* F. P. 667211; abst. C. A. 1930, **24**, 1227.

5. *Ibid.* Can. P. 293735.

6. *Ibid.* E. P. 313233; abst. C. A. 1930, **24**, 865; J. S. C. I. 1929, **48**, 671-B; Chem. Zentr. 1929, II, 1590. E. P. 313234; abst. C. A. 1930, **24**, 865; J. S. C. I. 1929, **48**, 671-B; Chem. Zentr. 1929, II, 1590. E. P. 313235; abst. C. A. 1930, **24**, 865; J. S. C. I. 1929, **48**, 671-B; Chem. Zentr. 1929, II, 1590. F. P. 671346; abst. C. A. 1930, **24**, 2144. Can. P. 293734.



carbonyl chloride<sup>1</sup>. Cellulose derivatives of the above hydroxy-aliphatic acids are made by treating cellulose with glycollic, lactic or hydracrylic anhydrides (which may be prepared by treating the sodium or potassium salts of the acids with thionyl chloride). Mixer esters (cellulose glycolate-lactate as example) are obtained by using an admixture of anhydrides, or a combination of acetic anhydride with each of the above results in the formation of cellulose aceto-glycollate, acetolactate and aceto-hydracrylate. Details have been published<sup>2</sup> for the formation of cellulose alkoxyalkacyl derivatives (cellulose esters or alkoxy aliphatic acids) by reacting upon cellulose with an alkoxyacetic acid alone or in the presence of an aliphatic acid, sulfuric acid, hydrochloric acid or ferric chloride being used as catalyst, and the esters being subjected to a subsequent partial hydration treatment. Where formic acid is the aliphatic acid used<sup>3</sup>, cellulose formyl-glycollate, formyllactate and formyl-hydracrylate are formed.

It has been found<sup>4</sup> that when cellulose is acylated with chlor- or brom-acetic anhydrides, mixed esters as the cellulose chlor-acetates result. The halogen may subsequently be replaced by hydroxyl, amino-, alkylamino- or other groups. In the production of insulators<sup>5</sup>, layers of cellulose ethers and esters are pressed together in a plastic condition. F. Hahn<sup>6</sup> prepares cellulose ethers by mixing finely ground cellulose with a slurry of NaOH in an inert or non-etherifiable liquid such as benzene, which facilitates

1. H. Dreyfus, E. P. 316160; abst. C. A. 1930, **24**, 1739; J. S. C. I. 1929, **48**, 848-B. F. P. 672235; abst. C. A. 1930, **24**, 2290.

2. *Ibid.* E. P. 314918; abst. C. A. 1930, **24**, 1507; J. S. C. I. 1929, **48**, 714-B. F. P. 671921; abst. C. A. 1930, **24**, 2290. Addn. 36814 to F. P. 671921; abst. C. A. 1931, **25**, 1082.

3. *Ibid.* E. P. 314919; abst. C. A. 1930, **24**, 1508; J. S. C. I. 1929, **48**, 714-B. F. P. 671103; abst. C. A. 1930, **24**, 1867. See E. P. 314918.

4. *Ibid.* E. P. 320842; abst. C. A. 1930, **24**, 2599; J. S. C. I. 1930, **49**, 379-B.

5. Dubilier Condenser Co., D. R. P. 482282; abst. C. A. 1930, **24**, 177.

6. E. I. Du Pont de Nemours & Co., E. P. 311697; abst. C. A. 1930, **24**, 960; J. S. C. I. 1930, **49**, 985-B.

subsequent alkylation and formation of a product suitable for film manufacture.

Cellulose ether compositions for lacquers and coating purposes are producable by the use together of solvents and non-solvents or "partial solvents"<sup>1</sup>, as gasoline and butyl alcohol, or a composition may be formed from ethylcellulose, rosin ester, blown linseed oil, butyl lactate, gasoline and a drier. As plasticizers for cellulose ethers and esters<sup>2</sup>, unsymmetrical diarylethanes have been patented, such as diphenylethane, ditolyethane, dixylyethane or dinitrodiphenylethane, being especially suitable for use with ethyl- and benzyl-cellulose. As non-discoloring plasticizing agents<sup>3</sup>, amyl acetate, ethyleneglycol diacetate, triacetin and not more than 12% of camphor have received patent protection.

In the dry-spinning of cellulose ether or ester artificial filaments<sup>4</sup>, especially of less than 3-4 deniers, spinning apertures of normal dimensions are used, but the cellulose solution contains a solvent or latent solvent and a coagulant having a boiling point higher than that of the solvent portion, the liquid components being so adjusted as to their relative speed of evaporation to permit of winding speeds greater than normal. A colored composition suitable for use on wood and metal<sup>5</sup> comprises a cellulose ester or ether, a plasticizer such as butyl tartrate, shellac or copal, furyl alcohol and a small amount of acid as sulfuric.

K. Freudenberg has found<sup>6</sup> that methylation of cellobiose and "biosan" fractions, give products of boiling point

1. E. I. Du Pont de Nemours & Co., E. P. 812309; abst. C. A. 1930, **24**, 960; J. S. C. I. 1931, **50**, 16-B; Brit. Plastics, 1931, **2**, #21, 432; Chem. Zentr. 1929, II, 3199. Can. P. 308108; abst. C. A. 1931, **25**, 1379.

2. *Ibid.* E. P. 312604; abst. C. A. 1930, **24**, 961; J. S. C. I. 1930, **49**, 780-B.

3. Du Pont Viscoid Co., E. P. 310475; abst. C. A. 1930, **24**, 703; J. S. C. I. 1931, **50**, 158-B; Chem. Zentr. 1929, II, 1841.

4. A. Eichengrün, E. P. 317408; abst. C. A. 1930, **24**, 2294; J. S. C. I. 1929, **48**, 848-B. Cites E. P. 243350.

5. C. Fawkes, U. S. P. 1732124; abst. C. A. 1930, **24**, 252; J. S. C. I. 1930, **49**, 26-B.

6. Naturwissenschaften, 1929, **17**, 959; abst. C. A. 1930, **24**, 1213; J. S. C. I. 1930, **49**, 198-B.

higher than octamethylcellobiose, and molecular weight corresponding to methylated tri-saccharide. In an endeavor to determine to what extent the benzene ring is present in lignin and whether its methoxyl group belongs to an aliphatic or aromatic system<sup>1</sup> a purified lignin of 17% methoxyl was used, and the action of hydrobromic acid upon it determined under various conditions. Methyllignin and methylcellulose were similarly treated. Methylcellulose gave as high as 34.8% MeO, and methyllignin 32%. He proved<sup>2</sup> that trimethylcellulose differs materially from 2.3.6-trimethylglucose.

In the ornamentation of tiles and statues<sup>3</sup>, the particles are first coated with a glazing liquid of water and finely ground cement together with small quantities of substances such as zinc soaps, for rendering the colloidal condition of the liquid more permanent; while this coating is still plastic there is applied to it a thin covering of a solution of a cellulose ether or ester with a coloring matter.

In the production of films<sup>4</sup>, the flowing solution of cellulose ether or ester is placed on a support, and after drying, receives an addition of glycerol or formaldehyde to avoid the formation of static electricity in the films.

K. Hess<sup>5</sup> in repeating the work of K. Freudenberg<sup>6</sup> dissolved the "insoluble" methylcellulose of Freudenberg in water at 0° and then extracted with methyl alcohol and chloroform (1:1). The non-identity of an anhydride of trimethylglucose with trimethylcellulose, for which the de-

1. K. Freudenberg, W. Belz and C. Niemann, Ber. 1929, **62B**, 1554; abst. C. A. 1929, **23**, 5038; J. S. C. I. 1929, **48**, 915-A; Chem. Zentr. 1929, II, 554.

2. K. Freudenberg, E. Bruch and H. Rau, Ber. 1929, **62B**, 3078; C. A. 1930, **24**, 1846; J. S. C. I. 1930, **49**, 198-A.

3. K. Friedrich and C. Friedrich, E. P. 309755; abst. C. A. 1930, **24**, 704; J. S. C. I. 1929, **48**, 520-B; Chem. Zentr. 1929, II, 2092.

4. A. Giebmanns, E. P. 344645; abst. J. S. C. I. 1931, **50**, 583-B. F. P. 670190, 670191, 670192, 670193, 670194, 670195, 670196; abst. C. A. 1930, **24**, 1979. Swiss P. 126780; abst. Kunst. 1929, **19**, 140.

5. K. Hess, Ber. 1929, **62B**, 924; abst. C. A. 1929, **23**, 4063; J. C. S. I. 1929, **48**, 684-A; Chem. Zentr. 1929, I, 2527.

6. Ber. 1929, **62**, 383; abst. J. S. C. I. 1929, **48**, 430-A.

pression in dilute solution corresponds with that of a trimethylglucosan, is considered as not a valid argument for or against the main valency chain structure of cellulose.

In the preparation of resists used in dyeing<sup>1</sup>, the material to be dyed is printed with a mixture of an oxidizing agent such as sodium bichromate or sodium *m*-nitrobenzenesulfonate and an aqueous solution of methylcellulose, dried, and dyed in vat liquor. In the manufacture of ethylbenzylcellulose, ethyl chloride is used to react upon alkalicellulose, then 2 mols. benzyl chloride being added for every 10-12 mols. ethyl chloride used<sup>2</sup>. The alkylation is carried on at such temperatures and pressures at which a saponification of excess of alkylating agents to free acid is avoided. Diethylbenzylcellulose apparently is formed.

In preparing cellulose ethers according to the O. Leuchs and E. Dorr process<sup>3</sup>, water is removed during the etherification and sodium hydroxide added to the alkylation mixture of alkalicellulose and ethyl chloride, the water being absorbed by solid NaOH. In the formation of cellulose ethers and ester-ethers<sup>4</sup>, cellulose is heated at around 100° in the presence of a base such as pyridine, with a number of fatty acid halides, either in admixture or successively. They may be replaced wholly or in part by a halide of a cyclic-substituted fatty acid (phenylacetic acid) or of an alicyclic carboxylic acid (cyclohexanecarboxylic acid). The above reaction may be carried out with a cellulose ether instead of cellulose, in which only a portion of the replaceable hydrogens in the cellulose ether have been etherified. Ethylcellulose phenylacetate or methylcellulose cyclohexane-

1. J. Höpker, U. S. P. 1730211; abst. C. A. 1929, **23**, 5597; J. S. C. I. 1929, **48**, 938-B.

2. I. G. Farbenindustrie, A. G., Can. P. 293163.

3. U. S. P. 1694127; abst. C. A. 1929, **23**, 981; J. S. C. I. 1929, **48**, 353-B; Chem. Zentr. 1929, I, 1635. E. P. 306857; abst. C. A. 1929, **23**, 5317; J. S. C. I. 1929, **48**, 353-B. See E. P. 286789, 288143.

4. *Ibid.* E. P. 305947; Addn. to E. P. 283131, 297766; abst. C. A. 1929, **23**, 5041; J. S. C. I. 1930, **49**, 814-B; Brit. Patents, 1930, **2**, #17, 229; Chem. Zentr. 1929, II, 112. E. P. 305661; abst. C. A. 1929, **23**, 4818. See E. P. 284298, 292929.

carboxylate are examples. Ether-esters of cellulose may also be prepared<sup>1</sup> by the acetylation (for instance) of monoethylcellulose or methylcellulose, methyl (or ethyl)-cellulose acetate being formed.

Water-insoluble cellulose ethers as ethylcellulose, may be purified by extraction with a mixture of water and a water-soluble solvent such as acetone<sup>2</sup>, to remove components of the material which are of low viscosity and swell in water. Solutions of cellulose ethers are capable of stretch-spinning by including in the solvent mixture an ingredient which is only extractable with difficulty by the precipitating bath. Thus the solvent may be a mixture of ethyl alcohol and carbon tetrachloride, the precipitating bath being a solution of calcium chloride<sup>3</sup>.

It is claimed that artificial silk which is fast to boiling may be produced by dry-spinning a water-insoluble cellulose ether from which substantially all the constituents of low viscosity which swell in water have previously been removed<sup>4</sup>. In transferring designs to wood, metal or other surfaces<sup>5</sup>, especially graining, the transferable layer coming into contact with the surface to be decorated, comprises a cellulose ether solution with resins, both being soluble in alcoholic solvents.

While photographic film spools are usually made by die-casting methods of metals as aluminum, it has been found that cellulose ethers or ether-esters may be used for the same purpose with advantage<sup>6</sup>. Anhydrous lacquers containing cellulose ethers or esters<sup>7</sup>, with addition of suit-

1. I. G. Farbenindustrie, F. P. 671110; abst. C. A. 1930, **24**, 1979.

2. I. G. Farbenindustrie, A. G., E. P. 321651; abst. C. A. 1930, **24**, 2882; J. S. C. I. 1930, **49**, 99-B; Cellulose 1930, **1**, #7, 198. D. R. P. 511019; abst. C. A. 1931, **25**, 1379.

3. *Ibid.* D. R. P. 487024; abst. C. A. 1930, **24**, 2292.

4. *Ibid.* E. P. 322730; abst. C. A. 1930, **24**, 2882; J. S. C. I. 1930, **49**, 319-B; Silk J. and Rayon World, **1930**, **6**, #70, 62. See E. P. 321651.

5. *Ibid.* E. P. 317871; abst. C. A. 1930, **24**, 2258; J. S. C. I. 1929, **48**, 863-B; Brit. Plastics, 1929, **1**, #6, 234.

6. *Ibid.* E. P. 316302; abst. C. A. 1930, **24**, 1589. F. P. 678459.

7. *Ibid.* E. P. 318567; abst. C. A. 1930, **24**, 2316; J. S. C. I. 1929, **48**, 1047-B.

able solvents and pigments, may be printed by means of deeply engraved plates or rollers on non-resilient bases, which may be rendered smooth and even by previous application of a lacquer coating.

In the manufacture of plastic compositions<sup>1</sup>, water-insoluble or difficulty soluble binders as ethylcellulose are formed into an aqueous dispersion which is sprayed, kneaded or otherwise brought into the desired form, and then may be dried and treated with substances capable of dissolving or swelling the binding agent. As example, 100 parts water-insoluble ethylcellulose is made into a paste with 150 of ultramarine blue by means of a solution of 1 of sodium butylnaphthalenesulfonate in 50 of water. In the preparation of rubber compositions<sup>2</sup>, sheets for use in the same manner as linoleum, celluloid and horn are made from synthetic rubber (such as that from isoprene) with cellulose ethers included with other materials.

Lacquers giving white or colored mat effects are obtained by dissolving a plastic mass comprising a cellulose ether and a high-boiling hydrocarbon, fat or oil<sup>3</sup>, in a mixture of liquids of which one is a solvent for both the cellulose ether and the hydrocarbon, while the other is a solvent for the cellulose ether only. Example, a composition of ethylcellulose and a condensation product of xylyl chloride and naphthalene is dissolved in a mixture of benzene and ethyl alcohol. Lacquers may also be produced<sup>4</sup> by dissolving a cellulose ether and a heavy metal salt of an acid of high molecular weight (aluminum palmitate, zinc stearate) in a solvent combination harmonious to both, a softening agent being added. Or the lacquer may contain

1. I. G. Farbenindustrie, E. P. 319371; abst. C. A. 1930, **24**, 2558.

2. *Ibid.* E. P. 304612; abst. C. A. 1929, **23**, 4848; J. S. C. I. 1930, **49**, 677-B; Chem. Zentr. 1929, I, 2494.

3. *Ibid.* E. P. 309194; abst. C. A. 1930, **24**, 509; J. S. C. I. 1930, **49**, 859-B; Silk J. 1929, **6**, #63, 66; Chem. Zentr. 1929, II, 657. D. R. P. 479083; abst. C. A. 1929, **23**, 4836; Chem. Zentr. 1929, II, 1480. Compare D. R. P. 365169, 336476.

4. *Ibid.* Can. P. 290806.

an oxyn such as linoxyn<sup>1</sup> combined with a cellulose ether as ethyl- or benzyl-cellulose.

In the tanning and stuffing of leather<sup>2</sup>, the liquor is prepared by agitating a fat or oil such as train oil, neat's-foot oil, bone oil, mineral oil or wool fat with an aqueous solution of an alkylcellulose as dimethylcellulose. Wetting agents as sodium dibutyl-naphthalenesulfonate and solvents as carbon tetrachloride may be added. In the production of rubber pastes<sup>3</sup>, it has been found that a paste which can be homogeneously mixed with fillers and vulcanizing agents may be prepared from natural or synthetic latex by treatment with a water-soluble cellulose ether such as methylcellulose, or a solution of the ether, to form a precipitate, then separating the precipitate from the water. Example, 100 of natural rubber latex (preserved with ammonia) containing 20% rubber, is incorporated with 2 of water-soluble methylcellulose. Upon heating to 55°, both rubber and cellulose ether separate, and on diluting with cold water a rubber milk is again obtained.

In the formation of waterproof articles from alkylcellulose<sup>4</sup>, a mixture of an aqueous solution of methylcellulose with a colloidal substance (drying oil or aldehyde condensate) is made into the desired shape, then heated to convert the latter into a sparingly soluble or insoluble state. Artificial porous substances are prepared by incorporating organic plastifiable materials as cellulose ethers, with casein, waxes or resins, and with substances which produce gas on heating or expansion<sup>5</sup>. The decomposition

1. I. G. Farbenindustrie, E. P. 307361; abst. C. A. 1929, **23**, 5338; J. S. C. I. 1930, **49**, 780-B; Brit. Plastics, 1930, **2**, #17, 101; Chem. Zentr. 1929, II, 100. F. P. 670762; abst. C. A. 1930, **24**, 1996.

2. *Ibid.* E. P. 318070; abst. C. A. 1930, **24**, 2326; J. S. C. I. 1929, **48**, 950-B.

3. *Ibid.* E. P. 305490; abst. C. A. 1929, **23**, 4848; J. S. C. I. 1930, **49**, 730-B; Chem. Zentr. 1929, I, 2929. F. P. 668907; abst. C. A. 1930, **24**, 1764.

4. *Ibid.* E. P. 308284; abst. C. A. 1930, **24**, 239; J. S. C. I. 1929, **48**, 595-B; Brit. Plastics, 1929, **1**, #3, 113; Chem. Zentr. 1929, II, 1103.

5. *Ibid.* F. P. 668142; abst. C. A. 1930, **24**, 1477. E. P. 242274; abst. J. S. C. I. 1927, **46**, 612-B; Chem. Zentr. 1926, I, 2971.

of the gas-forming substance may be brought about by submitting the mixture to a pressure and then to expansion in an extrusion press, preferably at a slightly elevated temperature.

In the formation of cold frames and similar transparent roofings for greenhouses<sup>1</sup>, sheets of transparent material are used comprising cellulose ethers and urea-formaldehyde condensation products, strengthened by an imbedded network. Cellulose ethers made from lignin and containing 1.5-2.5 alkyl groups per molecule of cellulose are rendered resistant to the action of water by employing in the alkylation 2 mols. of an alkylating agent as benzyl chloride for each 10-30 mols. alkylating agent as ethyl chloride. An alcohol-benzene soluble ether is thus obtained from pasteboard pretreated with a 50% NaOH solution and ripened<sup>2</sup>. Ethylbenzyl lignin is formed. In the manufacture of products resembling celluloid<sup>3</sup>, cellulose ethers are incorporated with a neutral phosphoric ester containing at least one radical of a primary aliphatic alcohol with more than 4 carbon atoms, the remainder belonging to the aliphatic or hydroaromatic series, e.g., triamyl, di-isoamyl-cyclohexyl, and diisoamylbutyl phosphates being examples.

By the treatment of abietic or adipic acids with alkylene oxides, hydroxyalkyl esters are obtained<sup>4</sup> which are excellent softeners for the cellulose ethers. Ethylene adipate and abietate and glyceryl adipate and abietate are examples. For the keeping soft of artificial resins capable of being hardened<sup>5</sup> a small amount of ethylcellulose incor-

1. I. G. Farbenindustrie, E. P. 306242; abst. C. A. 1929, **23**, 5019; J. S. C. I. 1929, **48**, 298-B; Chem. Zentr. 1929, II, 512.

2. *Ibid.* E. P. 305946; abst. C. A. 1930, **24**, 5040; J. S. C. I. 1930, **49**, 414-B; Chem. Zentr. 1929, II, 111. F. P. 669256; abst. C. A. 1930, **24**, 1740. D. R. P. 492062; abst. C. A. 1930, **24**, 2599.

3. *Ibid.* E. P. 308395; abst. C. A. 1930, **24**, 239; J. S. C. I. 1929, **48**, 594-B; Brit. Plastics, 1929, **1**, #1, 36; 1929, **1**, #3, 113; Chem. Zentr. 1929, II, 814. F. P. 674118; abst. C. A. 1930, **24**, 2601; Nitrocellulose, 1931, **2**, 104. See also F. P. 656151.

4. *Ibid.* E. P. 328190; abst. C. A. 1930, **24**, 5518; J. S. C. I. 1930, **49**, 677-B. F. P. 662603; abst. C. A. 1930, **24**, 516.

5. *Ibid.* E. P. 315835. Ital. P. 262866. Argentine P. 30974.



porated therewith is said to keep them soft indefinitely. Condensation products from crude naphtha and alkylaryl ethers of the type  $3.5\text{-R}'\text{R}''\text{-C}_6\text{H}_3\text{OR}$ , in which R and R' are the same or different alkyl groups and R'' an alkyl group, are made by treating a mixture of crude naphtha and the ether with a polymerizing agent (other than aluminum chloride) as stannic chloride, borofluoracetic acid or sulfuric acid. The products formed are claimed as particularly useful in making lacquers containing cellulose ethers<sup>1</sup>.

Cellulose ethers or esters are dyed with 4-amino-1.8-naphthalimides carrying as substituent in the imide group a hydroaromatic residue, e.g., the cyclohexyl derivative, m. pt.  $240\text{-}242^\circ$  (4-amino-1.8-naphthalic acid cyclohexylimide)<sup>2</sup>. In dyeing cellulose ethers<sup>3</sup>, isocyclic bases (hexahydro-aniline, -ethylaniline, -methylaniline, -toluidines, -xylidine, or -1.7-naphthylenediamine) or their salts are used with acid dyes (Orange II, Benzo Brown G, Rhoduline Red NO, Methylene Blue, Bismark Brown FR, Saffranine FF), whereby deeper shades are obtained than without them.

Alkoxyanthraquinones without further substituents in the nucleus or in the alkyl group are suitable dyes for cellulose ethers and esters<sup>4</sup>, and are applied in aqueous dispersions. Examples, 1.4-dimethoxyanthraquinone (golden-yellow), 1.4.5-trimethoxyanthraquinone (greenish yellow). Cellulose ethers may also be dyed with alkylthiolanthraquinones, e.g., ethylthiolanthraquinone (yellow), 1.4-di-(ethylthiol) anthraquinone (orange), 1-amino-4-ethyl-

1. I. G. Farbenindustrie, E. P. 314810; abst. C. A. 1930, **24**, 1530.

2. *Ibid.* E. P. 328308; Addn. to E. P. 304739; abst. C. A. 1930, **24**, 5510; J. S. C. I. 1930, **49**, 709-B. F. P. 667983; abst. C. A. 1930, **24**, 1522.

3. *Ibid.* F. P. 656995; abst. C. A. 1929, **23**, 4351. E. P. 293766; abst. C. A. 1929, **23**, 1759; J. S. C. I. 1930, **49**, 185-B; Chem. Zentr. 1928, II, 2064. See Schultz, "Farbstofftabellen" 6th Ed. 1923, No. 145.

4. *Ibid.* E. P. 307813; abst. C. A. 1930, **24**, 248; J. S. C. I. 1929, **48**, 639-B; Chem. Zentr. 1929, II, 1224.

thiolanthraquinone (bordeaux), 1-methylamino-2-ethylthiolanthraquinone (pink), 1-amino-2-isopropylthiolanthraquinone (red), and 1-methylamino-2-isobutylthiolanthraquinone (pink)<sup>1</sup>. Cellulose ethers are dyed deep greenish yellow tints by treatment with compounds obtained by interaction of the anhydride of 4-amino-1.8-naphthalic acid with ammonia or suitable amine; examples being 4-amino-1.8-naphthalic acid-ethylimide, or 4-amino-1.8-naphthalic acid 2'-methylphenylimide<sup>2</sup>.

In dyeing vegetable fibers, the goods are impregnated with an ether of 2.3-hydronaphthoyl-2-amino-3-naphthol, and the color is developed with suitable diazo, tetrazo or diazoazo compounds<sup>3</sup>. Example, cotton is impregnated with 2.3-hydroxynaphthoyl-2-amino-3-naphthol methyl ether and the color developed with the diazo solutions from 4-nitro-1.2-anisidine and 5-chlor-1.2-toluidine respectively. In producing colored designs on textiles<sup>4</sup> they are treated with substances convertible into dyes, or with dyes having little affinity for the fibers, while unevenly applying moisture and/or heat. It is then found that the intermediate or dye distributes itself unevenly over the textile, deeper shades resulting at warmer and wetter parts than at colder and drier. In treating wool or animal fibers it may be desirable to inhibit the affinity of the fibers for dyes by bringing on to the fibers cellulose ethers or esters or starch.

Fast shades on goods composed of cellulose ethers or esters are obtained<sup>5</sup> with aminoanthraquinones or their

1. I. G. Farbenindustrie, E. P. 308242; Addn. to E. P. 307813; abst. C. A. 1930, **24**, 248; J. S. C. I. 1929, **48**, 938-B; Chem. Zentr. 1929, II, 1224.

2. *Ibid.* E. P. 304739; abst. C. A. 1929, **23**, 4831; J. S. C. I. 1930, **49**, 506-B; Chem. Zentr. 1929, I, 2924. F. P. 646371; abst. C. A. 1929, **23**, 2305.

3. *Ibid.* D. R. P. 470537; abst. C. A. 1929, **23**, 1759; Chem. Zentr. 1929, I, 2701.

4. *Ibid.* D. R. P. 472474; abst. C. A. 1929, **23**, 2581; Chem. Zentr. 1929, I, 2827. In this connection see D. R. P. 291076, 424981. Schultz, "Farbstofftabellen" 6th Ed. 1923, No. 10, 23, 145, 214, 227, 307, 319, 424, 539, 543.

5. R. Heidenreich, D. R. P. 473454; abst. C. A. 1929, **23**, 3110; Chem. Zentr. 1929, I, 2827. See D. R. P. 348530.

derivatives when the dyeing is performed in the presence of a sulfurized phenol, examples being the use of  $\alpha$ -aminoanthraquinone, 1,4-diaminoanthraquinone, 1,4-5,8-tetraminoanthraquinone and  $\alpha$ -methylaninoanthraquinone. Fast red to blue shades are produced<sup>1</sup> by dyeing with ethers of 1,4-diamino-2-hydroxyanthraquinone or its N-substituted derivatives (e.g., 2-ethoxy-1,4-diaminoanthraquinone). In dyeing and printing cellulose ethers and esters<sup>2</sup>, condensation products of aliphatic amines with naphthazarin are used, trimonomethylaminoanthraquinone being an example.

The dyeing of cellulose ethers and esters may be carried on<sup>3</sup> by adding isocyclic bases to the dyebath instead of pyridine or its hydrogenation products previously described. Thus hexahydroaniline is added to a dyebath of sodium 1-amino-4-hexahydroanilidoanthraquinone-2-sulfonate, blue dyeings resulting. Orange II, Benzo Brown G, and Rhoduline Orange NO are also used. H. Dreyfus<sup>4</sup> has described a new series of cellulose derivatives obtained by etherifying the hydroxyl groups of cellulose hydroxyalkyl ethers (hydroxyalkylcelluloses), ethyl-tri-(trihydroxyethyl)cellulose being given as an example. He makes textiles of cellulose ethers more resistant to the action of de-lustering agents<sup>5</sup> by incorporating with the ether an agent having a solvent or swelling action on the ether and submitting them to a steaming operation. Suitable agents include resorcinol, hydroquinone, cresols, diacetone alcohol, diacetin, diethyl tartrate and phthalimide.

Cellulose esters and ethers may be dyed by 1-amino-4-arylaminoanthraquinone or its arylamino substituted deri-

1. P. Nawiasky, D. R. P. 479225; abst. C. A. 1929, **23**, 4831; Chem. Zentr. 1929, II, 2506. E. P. 272482.

2. R. Metzger and P. Nawiasky, D. R. P. 485265; abst. C. A. 1930, **24**, 973. See D. R. P. 447420.

3. I. G. Farbenindustrie, A. G., D. R. P. 486696; Addn. to D. R. P. 439004; abst. C. A. 1930, **24**, 1521. See D. R. P. 445979. Schultz, "Farbstofftabellen" 6th Ed. 1923, No. 145.

4. F. P. 37753; Addn. to 629099; abst. C. A. 1931, **25**, 4705.

5. F. P. 686644, Addn. 37856; abst. C. A. 1931, **25**, 605, 4719.

vatives<sup>1</sup>. Examples, 1-amino-4-anilineanthraquinone (blue). The aniline group in the above may be replaced by *p*-toluino, *b*-naphthylamine and *p*-acetylaminoaniline groups.

Dull effects are obtained on cellulose ethers and esters or their transformation products<sup>2</sup> by applying solutions containing urea or its derivatives, vaporizing, washing and drying. A thickening agent as tragacanth may be added to the solution. In preparations for printing, painting, coating or impregnating surfaces<sup>3</sup>, cellulose esters or ethers are used in water-soluble formic acid esters (glycol monoformate, glycol diformate, propylene glycol diformate, 1,3-butylene glycol monoformate). In order to simultaneously fix a printed vat dye and a printed aniline black, the vat dye is used in admixture with a cellulose ether or ester capable of being precipitated by an alkali, and after printing<sup>4</sup>, the aniline black is developed, the material is treated in an alkaline bath containing a reducing agent, the vat dye being fixed by steaming. Colored reserves on aniline black are obtained by using a vat-dye paste thickened with cellulose ethers or esters<sup>5</sup>, to which a reserving agent (sodium acetate, sodium hydrogen sulfite, zinc oxide) is added.

In the production of colored compounds on cellulose ether filaments or textiles<sup>6</sup>, naphthazarin is treated at 50-60° in presence of zinc dust or boric acid with an aliphatic amine. Methylamine yields 2,8-di(methylamino)-5-hydroxy-1,4-naphthaquinone, and 2,5,8-tri(methylamino)-1,4-naphthaquinone, separable by means of chlorobenzene. The triamino compound gives blue-green, or with *p*-nitro-

1. I. G. Farbenindustrie, A. G., D. R. P. 487941; abst. C. A. 1930, **24**, 1991. F. P. 667983; abst. C. A. 1930, **24**, 1522.

2. *Ibid.* F. P. 672217; abst. C. A. 1930, **24**, 2291; D. R. P. 512399; abst. C. A. 1931, **25**, 1393.

3. *Ibid.* E. P. 311795; abst. C. A. 1930, **24**, 981; J. S. C. I. 1929, **48**, 609-B; Brit. Plastics, 1929, **1**, 114.

4. *Ibid.* E. P. 311779; abst. C. A. 1930, **24**, 974; J. S. C. I. 1930, **49**, 815-B; Chem. Zentr. 1929, II, 2507.

5. *Ibid.* E. P. 311740; abst. C. A. 1930, **24**, 974; J. S. C. I. 1930, **49**, 815-B; Chem. Zentr. 1929, II, 2831.

6. *Ibid.* E. P. 304804; abst. J. S. C. I. 1929, **48**, 317-B; Chem. Zentr. 1929, I, 2926. F. P. 655167; abst. C. A. 1929, **23**, 4083.

aniline + *b*-hydroxyethyl-*m*-toluidine and 1.4-aminohydroxyanthraquinone, black shades.

Fabrics may be printed with vat dyes and a cellulose ether (methylcellulose)<sup>1</sup>, and then passed through an alkaline hydrosulfite bath. The cellulose ether is thus precipitated and the dye does not bleed, even if the fabric is not dried before steaming. If it is desired to *promote* bleeding or running in dyeing piece goods<sup>2</sup>, an agent is applied in the padding process to assist penetration of the dye. For this purpose an alkali salt of carboxymethylcellulose (made by condensation of alkalicellulose with chloracetic acid) capable of forming neutral or alkaline colloidal solutions in water may be used. In printing fabrics with vat dyes<sup>3</sup> a stable reducing agent as glucose or a ferrous or stannous salt is added to the printing paste thickened with a cellulose ether; the thickened fabric being subsequently treated in an alkaline bath and then steamed.

Films and fibers have been described<sup>4</sup> made from solutions of cellulose ethers and esters in which carbon bisulfide is an essential ingredient in the mixture of solvents used. Thus, films of 20-25% greater solidity and tensile strength than films from benzene with the same extensibility, are claimed to result from an 8% solution of triethylcellulose in a mixture containing carbon bisulfide 92, benzene 8. Films with 3 times the extensibility of those from acetone solution and the same solidity are obtained from a 7% solution of triethylcellulose in a mixture of CS<sub>2</sub> 96, acetone 4.

Cellulose ethers are precipitated from their solutions to form films<sup>5</sup>, by using solvents which have a high solu-

1. I. G. Farbenindustrie, E. P. 304787; Addn. to E. P. 279864; abst. C. A. 1929, **23**, 4831; J. S. C. I. 1930, **49**, 416-B; Chem. Zentr. 1929, II, 220.

2. *Ibid.* E. P. 305230; abst. C. A. 1929, **23**, 4830; J. S. C. I. 1930, **49**, 762-B; Chem. Zentr. 1929, II, 356. See E. P. 317117.

3. *Ibid.* E. P. 314904; Addn. to E. P. 279864; abst. C. A. 1930, **24**, 1522; J. S. C. I. 1930, **49**, 815-B; Chem. Zentr. 1929, II, 2507.

4. *Ibid.* F. P. 653297; abst. C. A. 1929, **23**, 3807; Chem. Zentr. 1929, II, 3261. Swiss P. 133158.

5. *Ibid.* F. P. 653583; abst. C. A. 1929, **23**, 3808; Chem. Zentr. 1929, I, 2940.

bility in the hydrocarbons which are used in the precipitating baths. In examples, solutions of ethylcellulose in carbon bisulfide and ethyl ether, or carbon bisulfide and butyl alcohol, or carbon bisulfide and benzene, or ethyl ether and benzene are precipitated by a bath of paraffin oil at 15°. Cellulose triacetate or butyrate or cellulose ethers are used with resinous condensation products of aliphatic dibasic acids (succinic, maleic) and polyhydric alcohols (glycerol, glycols) or their hydroxyalkyl ethers<sup>1</sup>, or condensates of dibasic acids (phthalic) and polyhydric alcohols containing 4 to 6 hydroxy groups per molecule<sup>2</sup>. Or the condensates may be prepared from aromatic dibasic acids and glycols<sup>3</sup>, or aromatic dibasic acids with hydroxyalkyl ethers of trihydric alcohols. The above produce lacquers and varnishes when incorporated with the cellulose ethers by means of solvents harmonious to both<sup>4</sup>.

Cellulose mon-, di- or tri-acetate or the corresponding chloracetates, especially suitable for artificial filaments are obtained<sup>5</sup>, by treating viscose with acetic or chloracetic acids. Esters of carbohydrates soluble in organic agents, with higher fatty acids or cyclic carboxylic acids<sup>6</sup>, are made by swelling the carbohydrate in aqueous alkali hydroxide of at least 30% strength, and esterifying. Examples are given of the preparation of starch lauro-benzoate, cellulose laurate, the coconut oil fatty acid ester of agar-agar, cellulose lauronaphthenate, and starch phenylacetate. Wood is rendered water-proof by impregnation with cellulose trilaurate in methylene chloride, chloroform and ben-

1. I. G. Farbenindustrie, E. P. 322540; abst. C. A. 1930, **24**, 2905; J. S. C. I. 1930, **49**, 157-B.

2. *Ibid.* E. P. 322541; abst. C. A. 1930, **24**, 2905; J. S. C. I. 1930, **49**, 157-B.

3. *Ibid.* E. P. 322542; abst. C. A. 1930, **24**, 2905; J. S. C. I. 1930, **49**, 157-B.

4. *Ibid.* E. P. 322543; abst. C. A. 1930, **24**, 2905; J. S. C. I. 1930, **49**, 157-B.

5. *Ibid.* E. P. 312915. In this connection see D. R. P. 287955.

6. *Ibid.* F. P. 668686; abst. C. A. 1930, **24**, 1650. See E. P. 293316, 293757.

zene<sup>1</sup>, or starch laurate in the same solvent combination. In the manufacture of gummed paper<sup>2</sup>, rolls of paper or cloth have applied to the non-gummed side a layer of mixed cellulose ether-ester (ethylcellulose laurate) to prevent sticking.

Artificial coatings are made from solutions of cellulose ethers and cellulose esters of higher fatty acids, naphthenic acid, resin acids, or their metallic salts, cellulose laurate, cellulose trilaurate and ethylcellulose with linseed or wood oil, ceresin, stearic acid or carnauba wax being specified<sup>3</sup>. To prepare surfaces of wood or metal for the reception of cellulose varnish<sup>4</sup>, an intermediate coating of cellulose dilaurate with guttapercha or cellulose monoaceto-distearate with rubber has been put forward, dissolved in benzene, xylene, chlorbenzene or dichlormethane.

In the production of shades on materials made from or containing cellulose ethers and esters<sup>5</sup>, it has been found that bright green shades are produced with *N, N'*-dimethyl-indigo. It appears that the viscosity characteristics of the cellulose ethers and esters may be reduced while preserving their film-forming qualities<sup>6</sup>, by treatment with an acid gas or vapor such as hydrochloric acid, either alone or admixed with an inert gas, until about 0.1-1.5% of the acid has been adsorbed by the dry materials, and then permitting the latter to season either at room temperature or at elevated temperatures until the viscosity has dropped to the degree desired.

1. I. G. Farbenindustrie, F. P. 661435; abst. C. A. 1930, **24**, 483.

2. *Ibid.* F. P. 661039; abst. C. A. 1930, **24**, 213. E. P. 302588; abst. J. S. C. I. 1930, **49**, 185-B; Chem. Zentr. 1929, I, 2504.

3. *Ibid.* F. P. 660510; abst. C. A. 1930, **24**, 252.

4. *Ibid.* E. P. 317987; abst. J. S. C. I. 1929, **48**, 863-B; Brit. Plastics, 1929, **1**, 234.

5. Imperial Chemical Industries, Ltd., and A. Davidson, E. P. 312506; abst. C. A. 1930, **24**, 973; J. S. C. I. 1929, **48**, 678-B; Chem. Zentr. 1929, II, 2607. F. P. 675635; abst. C. A. 1930, **24**, 2896. See L. Ettinger and P. Friedlaender, Ber. 1912, **45**, 2074.

6. Imperial Chemical Industries, E. P. 313091.

In waterproofing paper articles such as shotgun cartridge cases<sup>1</sup>, solutions of methyl-, ethyl- or benzyl-cellulose are used in the dissolved condition, an example being ethyl-cellulose 12, kauri 6, benzene and toluene, 50 each. Anthraquinone dyes are made by condensing *p*-phenylenediamine with an anthraquinone derivative containing in the 1-position an amino or alkylamino group, and in the 4-, 5-, or 8-positions a halogen atom. Monoacyl derivatives of *p*-phenylenediamine may also be used, and the acyl groups subsequently removed by hydrolysis. The unsulfonated products dye the cellulose ethers bluish-green colors<sup>2</sup>.

In the fabrication of coating compositions according to the process of F. Hahn<sup>3</sup>, cellulose esters or ethers are combined in solution with dissolved resinous glyceryl benzoylbenzoate, resinous glyceryl trilactate, resinous monoethylin benzoylbenzoate or resinous glyceryl benzoylbenzoate. Resin-like materials capable of forming useful combinations with the cellulose esters and ethers for varnishes and lacquers<sup>4</sup>, result by heating monoethylin with benzoylbenzoic acid, monoethylin-, monopropylin-, monobutylin- or monomethylin-benzoylbenzoate, -dilactate, -pyruvate, -salicylate and -tartrate being claimed. Monoethylin-, monomethylin-, monopropylin- and monobutylin-phthalate and oxalate have also been patented for the same purpose<sup>5</sup>. As plastifying bodies and high boilers for use in conjunction with methyl-cellulose<sup>6</sup>, methyl, propyl, butyl, isobutyl, glycollate (but not ethyl glycollate) have also been advocated.

1. C. Burke and F. Hahn, E. P. 315227; abst. C. A. 1930, **24**, 1741; Chem. Zentr. 1929, II, 3095.

2. Imperial Chemical Industries, A. Shepherdson and W. Tatum, E. P. 315905; abst. C. A. 1930, **24**, 1745; J. S. C. I. 1929, **48**, 808-B; Chem. Zentr. 1929, II, 2511.

3. E. P. 316321; abst. C. A. 1930, **24**, 1754; Chem. Zentr. 1929, II, 3190.

4. Imperial Chemical Industries, E. P. 316322; abst. C. A. 1930, **24**, 1754; Chem. Zentr. 1929, II, 3190.

5. *Ibid.* E. P. 316323; abst. C. A. 1930, **24**, 1754; Chem. Zentr. 1929, II, 3190. See E. P. 302961.

6. *Ibid.* Australia P. 16635. J. Payman, H. Swann, W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 311664; abst. C. A. 1930, **24**, 961; J. S. C. I. 1929, **48**, 691-B.



In the manufacture of non-resinous esters of dibasic acids useful as plasticizers for cellulose ethers and esters<sup>1</sup>, there have been described combinations of a dibasic acid or anhydride (phthalic anhydride) which is heated below 140° with an ether of a polyhydric alcohol still containing free hydroxyl groups to give the acid ester, which is then heated below 160° with excess of an aliphatic alcohol to complete esterification. Examples are the acid phthalates, phthalates, succinates and oxalates of monoethylin, butylmonoethylin, dimonoethylin, monobenzylin, butylmonobenzylin, pentaerythrite, mannitol and sorbitol. Phthalic anhydride and glycerol monoethyl ether at 140° give a product which with butyl alcohol and hydrogen chloride at 160° yields *b*-hydroxy-*w*-ethoxy-*n*-propylbutyl phthalate. These compounds in conjunction with dibutyl phthalate and castor oil<sup>2</sup> produce cellulose ether softeners of a wide range of useful applications.

Softeners for cellulose ethers and esters of the acetal type<sup>3</sup> have recently assumed some prominence, and comprise the acetal of the methyl (or ethyl, propyl, butyl) ether of diethylene glycol, as they yield films of exceptional softness, flexibility and clarity. As a gas-retaining material for aircraft covering<sup>4</sup> has been proposed a fabric treated with a mixture of regenerated cellulose and rubber dispersed in an organic solvent, the fabric being afterwards treated with an aqueous solution of a soluble cellulose glycollate.

Opaque, washable playing cards are formed of plasticized cellulose ether or ester-ether compositions containing such fillers as zinc oxide, lithopone, titanium oxide, bismuth oxychloride or antimony oxide<sup>5</sup>. In the coating of

1. Imperial Chemical Industries, E. P. 316324; abst. J. S. C. I. 1931, **50**, 476-B. See U. S. P. 1774500.

2. *Ibid.* E. P. 316325; abst. C. A. 1930, **24**, 1754; Chem. Zentr. 1929, II, 3189.

3. E. I. Du Pont de Nemours & Co., E. P. 318980; abst. C. A. 1930, **24**, 2599.

4. I. Jacobsohn, U. S. P. 1706294, 1706295; abst. J. S. C. I. 1929, **48**, 554-B.

5. S. Klausner, Cellon Werke and A. Eichengruen, E. P. 304276; abst. C. A. 1929, **23**, 4819.

artificial threads<sup>1</sup>, the material is preliminarily treated with a substance which is either a solvent for the coating material (which may be a cellulose ether) or which is soluble in the solvent used for the coating, thus improving adhesion of the coating.

In the pretreatment of cellulose for etherification or esterification<sup>2</sup>, the water in the cellulose is partially replaced by a swelling material as diacetin (for acetylation), or glycerol or glycol when bodies like benzylcellulose are to be prepared, in which case the reaction is carried out in an alkaline solution.

The orifice through which the thread issues in a cell for the dry-spinning of artificial filaments<sup>3</sup> of cellulose ethers and esters, is preferably situated in the bottom of the cell, and in a direct vertical line below the spinning nozzle so that the thread passes directly from the spinning nozzle to the winding bobbin with as few changes in direction as possible. In another spinning method<sup>4</sup>, the apparatus comprises a spinning cell, means for dividing the cell into separate zones to be successively traversed by the spun thread passing through the cell, and a spinning nozzle located in one of the zones.

In the production of artificial threads from cellulose ethers and esters<sup>5</sup>, it has been found that dispersively acting substances (water, alcohols, formaldehyde, toluene) when added to cellulose derivatives, form a solution of uniform and minimum particle size, which after preheating to 40-50° may be dry-spun.

1. F. Klein, E. P. 313410; abst. C. A. 1930, **24**, 1229; J. S. C. I. 1931, **50**, 799-B.

2. F. Klein, E. P. 313538; abst. C. A. 1930, **24**, 1216.

3. M. Klein, E. P. 303056; abst. Silk J. 1929, **5**, #59, 74. See E. P. 283139, 292561.

4. M. Klein, U. S. P. 1767215; abst. C. A. 1930, **24**, 4390. F. P. 660365; abst. C. A. 1930, **24**, 239.

5. O. Kohorn & Co. and H. Schupp, E. P. 318151; abst. C. A. 1930, **24**, 2293; J. S. C. I. 1931, **50**, 388-B; Silk J. 1929, **6**, #67, 72. F. P. 680173; abst. C. A. 1930, **24**, 3902.

T. Lieser<sup>1</sup> claims that treatment of cellulose B with nitrosomethylurethane in methyl alcohol affords a mono-methylcellulose, insoluble in organic solvents, which swells in sodium hydroxide solution. Similar treatment of cellulose gives products containing 0.75% and 0.87% methoxyl respectively. Hydrolysis of the methylated cellulose first with 75% sulfuric acid at the ordinary temperature and then with hot 8% acid, gives dextrose and 2-methylglucose. This last compound is also obtained by hydrolysis of 3.4.6-triacetyl-2-methylmethylglucoside (obtained by methylation of 1-chlor-3.4.6-triacetylglucose<sup>2</sup> with methyl iodide and silver oxide), with 10% hydrochloric acid. The treatment of methylcellulose with a mixture of acetic acid and anhydride containing sulfuric acid at 25-30° for 7-20 days gives about 50% of cellobiose octa-acetate<sup>3</sup>, indicating that some of the glucose anhydride units in the original product are not methylated. No methylcellobiose acetate could be detected, being probably decomposed during acetolysis.

In the manufacture of artificial silk and films from cellulose derivatives<sup>4</sup>, a solution in sodium hydroxide solution is made of a hydroxyalkyl derivative of cellulose (dihydroxypropyl- or hydroxyethyl-cellulose), which is then shaped into the form desired and suitably coagulated to obtain a solid product. L. Lilienfeld<sup>5</sup> prepares cellulose ethers by employing a cellulose which has been subjected to a preliminary treatment with alkali and carbon bisulfide under such conditions that at least a substantial part of the product is

1. Ann. 1929, **470**, 104; abst. C. A. 1929, **23**, 3672; J. S. C. I. 1929, **48**, 799-A. Cf. T. Lieser, Ann. 1928, **464**, 43; abst. C. A. 1928, **22**, 4792. J. S. C. I. 1928, **47**, 742-B.

2. P. Brigl, Zts. physiol. Chem. 1922, **122**, 245; abst. J. S. C. I. 1922, **41**, 910-A.

3. T. Lieser, Ann. 1930, **483**, 132; abst. J. S. C. I. 1931, **50**, 74-A.

4. L. Lilienfeld, U. S. P. 1722928; abst. C. A. 1929, **23**, 4572. E. P. 231807, 231808; abst. C. A. 1925, **19**, 3592; J. S. C. I. 1925, **44**, 913-B; Chem. Zentr. 1926, I, 274. See U. S. P. 1722927, 1722928. E. P. 177810, 203346, 203347.

5. E. P. 318088; abst. C. A. 1930, **24**, 2291; J. S. C. I. 1929, **48**, 1011-B. See E. P. 269531. See Aust. P. 112620, 112623. Ital. P. 194918, 199196. Swiss P. 97634. F. P. 522931.

insoluble in water, whereby etherification is facilitated, especially in ethyl- and benzyl-cellulose formation. In the production of ethylcellulose<sup>1</sup>, he prepares crude viscose which is diluted with water and allowed to congeal in a water-bath. It is then dissolved in 50% NaOH, ethyl sulfate added, and the whole heated. Hot water is then added and the mixture acidified with dilute sulfuric acid when the ether is precipitated.

U. Mancini<sup>2</sup> has described an apparatus for spinning cellulose ether and ester filaments, comprising a supply pipe, a spinning nozzle rotatably mounted with respect to the supply pipe, and a feed pump fixed with relation to, but rotatable with the nozzle for regulating the supply of "colloidion." In the manufacture of films or pellicles from cellulose derivatives<sup>3</sup>, water is added to the mass during or after manufacture. The water may be extracted from the air by the addition to the mass of hygroscopic substances such as glycerol or glycol, or by treating the mass in an atmosphere of steam. Treatment with steam also renders the films inodorous<sup>4</sup>.

In the preparation of cellulose xanthamides (cellulose thiourethanes)<sup>5</sup>, reaction of ammonia or primary or secondary amines with solutions of alkalicellulose slowly yields gelatinous products the composition of which approximates to  $C_{12}H_{19}O_6.O.CS.NRR'$ . The cellulose thiourethane formed was insoluble in water or the usual solvents, dissolving in alkali hydroxide solution to a viscous product which slowly decomposed, regenerating cellulose.

1. L. Lilienfeld, D. R. P. 470142; abst. C. A. 1929, **23**, 2293; Chem. Zentr. 1929, I, 1528. This patent was applied for March 16, 1912, and issued Jan. 9, 1929.

2. U. S. P. 1809303; abst. C. A. 1931, **25**, 4403. E. P. 302993; abst. C. A. 1929, **23**, 4572. F. P. 660357; abst. C. A. 1930, **24**, 239. Can. P. 290517, 290518, 290519.

3. J. Michael A. G. für Chemische & Metallurgische Industrie, F. P. 668369; abst. C. A. 1930, **24**, 1509.

4. *Ibid.* F. P. 672517; abst. C. A. 1930, **24**, 2292.

5. T. Nakashima, Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 109. In this connection see L. Lilienfeld, E. P. 231800, 231801, 231802, 231805, 231806, 231807.

By the treatment of paper made from cotton which has been steeped in 40-50% sodium hydroxide solution with sufficient benzyl chloride in benzene or toluene<sup>1</sup>, dibenzylcellulose is obtained in quantitative yield in a single operation. If 10-20% sodium hydroxide solution is used, a mixture of monobenzylcellulose and unchanged cellulose is obtained, from which the latter may be removed by treatment with ammoniacal copper oxide solution. The solubility of the benzylcellulose in chloroform, benzene and carbon tetrachloride, and insolubility in ether, alcohol and water served as a means for purifying the product. Dibenzylcellulose may be converted into the tribenzyl ether by dissolving in benzyl chloride and heating with silver oxide<sup>2</sup>. When a 1,4-diamino-2-hydroxyanthraquinone compound is treated with formaldehyde in the presence of sulfuric acid, a nitro group introduced into the resulting product, the nitrated product treated with water, and the nitro group reduced<sup>3</sup>, the formation of a dyestuff results which colors cellulose ethers and esters fast red to blue shades.

By the action of *p*-chlorbenzyl chloride and 2,4-dinitrochlorobenzene on alkalicellulose<sup>4</sup>, the lower *p*-chlorbenzylcellulose and 2,4 dinitrophenylcellulose have been obtained. It is possible to produce the latter still retaining the fibrous cellulose structure with a low nitrogen content. Reduction, diazotization and coupling results in a fiber in which the color is an integral part of the structure. Under suitable conditions, etherification with *p*-chlorbenzyl chloride may proceed to two-thirds of the theoretical.

1. T. Nakashima, Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 261; Abstracts, 1929, **2**, 31; abst. C. A. 1929, **23**, 3572; J. S. C. I. 1929, **48**, 684-A. See Chem. Zentr. 1929, I, 1678, 1679. T. Nakashima, Sci. Papers Inst. Phys. Chem. Research Tokyo, 1929, **12**, 121; abst. C. A. 1930, **24**, 721; J. S. C. I. 1930, **49**, 72-A.

2. T. Nakashima and I. Sakurada, Bull. Inst. Phys. Chem. Research Tokyo, 1929, **8**, 272; Abstracts, 1929, **2**, 33; abst. C. A. 1929, **23**, 3572; J. S. C. I. 1929, **8**, 684-A.

3. P. Nawiasky, U. S. P. 1736088; abst. C. A. 1930, **24**, 732.

4. H. Niethammer and W. Koenig, Cellulosechem. 1929 **10**, 201; abst. C. A. 1930, **24**, 3641; J. S. C. I. 1930, **49**, 72-A.

E. Pfeffer<sup>1</sup> has described a method for printing on fabrics with vat dyes, in which the latter are mixed with cellulose ethers as methylcellulose and the material subsequently treated with a reducing agent such as Rongalite C and potassium carbonate, being finished by the usual method of drying, steaming, washing and soaping. In a spectrographic investigation of cellulose derivatives<sup>2</sup>, curves for ethylcellulose and cellulose acetate have been obtained between 4000 and 2200 Å. by the Baly-Hartley method. In a method for the preservation of dyes in a fine state of subdivision<sup>3</sup>, an alkylcellulose such as methylcellulose is incorporated with insoluble or difficultly soluble dyes at the time of their production or shortly thereafter. C. Rivise<sup>4</sup> has summarized cellulose plastics in the pulp and paper industry.

G. Frank<sup>5</sup> produces artificial filaments from spinning solutions of cellulose ethers and esters by combining therewith partly polymerized organic compounds such as polymerized ethyl acrylate, vinyl acetate or metastyrol. By the action of allyl bromide on cotton cellulose suspended in 40-50% sodium hydroxide, di- and tri-allylcellulose has been prepared<sup>6</sup>. The addition of bromine showed that the double linking remained intact, diallylcellulose tetrabromide being obtained practically pure. The highly alkylated products were partially soluble in organic solvents, the purified ether being unchanged when heated at 210°. Knitted fabrics of

1. U. S. P. 1710007; abst. C. A. 1929, **23**, 2836; J. S. C. I. 1929, **48**, 470-B; Chem. Zentr. 1929, II, 2507. E. P. 279864; abst. C. A. 1928, **22**, 3051.

2. B. Rassow and W. Aehnelt, Cellulosechem. 1929, **10**, 169; abst. C. A. 1930, **24**, 3711; J. S. C. I. 1930, **49**, 10-A.

3. F. Risse and E. Fischer, U. S. P. 1719944; abst. C. A. 1929, **23**, 4347; J. S. C. I. 1929, **48**, 712-B. See U. S. P. 1730211.

4. Plastics, 1929, **5**, 261.

5. Röhm & Haas, A. G., and R. Herzog, E. P. 311784; abst. C. A. 1930, **24**, 962. F. P. 681156; abst. C. A. 1930, **24**, 4391. See E. P. 308284.

6. I. Sakurada, Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 114; abst. C. A. 1929, **23**, 3572; J. S. C. I. 1929, **48**, 430-A; Zts. ang. Chem. 1929, **42**, 549; Chem. Zentr. 1929, I, 1679.

cellulose ethers are treated with a solvent or swelling agent to effect a union of the interlacing loops and hold the latter permanently in place<sup>1</sup>.

It is claimed that when an aqueous cellulose of methyl-cellulose which in general has a tendency to coagulate<sup>2</sup>, is mixed with an acidified solution of diazotized *p*-aminodiphenylamine and 1.8-aminonaphthol-3.6-disulfonic acid, such solutions remain clear for an indefinite period. H. Sessler<sup>3</sup> alkylates cellulose (as with methyl sulfate) while the alkylating agent is in a gaseous form and at diminished atmospheric pressures in order to lower the temperature of alkylation with a corresponding lessening of danger of degrading the cellulose.

Absorbent fabrics suitable for wash cloths, towels and napkins formed of woodpulp, and withstanding washing without disintegration<sup>4</sup>, are prepared by the use of a discontinuous coating of a cellulose ether or ester. Slavo<sup>5</sup> has given an outline of the preparation of methyl- and ethyl-cellulose and of their possibilities as textiles. Cinematographic or other films may be formed by coagulating a solution of a cellulose ether while in the form of a film produced by surface tension between supports such as tapes, wires or threads, which may serve as marginal supports for the finished films<sup>6</sup>.

In the manufacture of continuous lengths of bodies which are hollow, contain gaseous bubbles or have a tubular

1. R. Sallmann and Raduner & Co., A. G., E. P. 309153; abst. C. A. 1930, **24**, 511. See E. P. 2718, 1892; 224077.

2. M. Schmidt and W. Krieger, U. S. P. 1756400; abst. C. A. 1930, **24**, 2959; J. S. C. I. 1930, **49**, 588-B. E. P. 311196; abst. C. A. 1930, **24**, 796; J. S. C. I. 1929, **48**, 624-B; Chem. Zentr. 1929, II, 3096. D. R. P. 470731.

3. U. S. P. 1704304; abst. C. A. 1929, **23**, 2033; *Plastics*, 1929, **5**, 515; Chem. Zentr. 1929, I, 2938.

4. M. Shoemaker, U. S. P. 1786781; abst. C. A. 1931, **25**, 813. E. P. 317330; abst. C. A. 1930, **24**, 2296; J. S. C. I. 1930, **49**, 708-B. F. P. 679615; abst. C. A. 1930, **24**, 3911.

5. Russa, 1929, **4**, 1003; abst. C. A. 1929, **23**, 4818; Chem. Zentr. 1929, II, 2523.

6. Societe des Usines Chimiques Rhone-Poulenc, E. P. 318250; abst. C. A. 1930, **24**, 2290. F. P. 688200; abst. C. A. 1931, **25**, 815.

structure from solutions of cellulose ethers<sup>1</sup>, one or more threads or solid film supports, which may or may not have the same composition as the cellulose derivative, are coated with the solution and the whole is heated so as to cause ebullition of the volatile solvent. The supports may remain imbedded in the manufactured product or may be separated. In the preparation of basic cellulose ethers<sup>2</sup>, alkal cellulose is treated with an amino or substituted amino-alkyl halide, the product being subsequently acylated or etherified, by known methods. The cellulose ethers or ether-esters may be converted into threads which have affinity for acid or direct dyes. Suitable basic etherifying agents are chlor-ethyldiethylamine in acetone, chlorethyldiethylamine hydrochloride or chlorethylethylaniline, producing such bodies as diethylaminoethylcellulose.

Fabric and filaments made from cellulose ethers or esters<sup>3</sup> may be delustered and rendered opaque by treatment with aqueous emulsions or suspensions of substances having a solvent or wetting action on the cellulose compound, temperature of treatment being between 40-80°. Suitable swelling agents are cyclohexanone, cyclohexanol, di- and tri-acetin, methyl phthalate, ammonium acetate, anisol, phenetole, nitrobenzene, ethyl benzoate, ethyl acetylacetate, benzyl alcohol, nitroanisols, nitrophenetols, guaiacol, benzaldehyde, salicylic aldehyde and amyl acetate.

Black shades are obtained directly on cellulose ethers and esters by means of disazo dyes of the type:- amine of the benzene series + *a*-naphthylamine or Cleve acid + 1.5-aminonaphthol, or 1.5-naphthylaminodiamine. As first components are mentioned aniline, *o*- and *p*-toluidine, *m*-xyli-

1. Societe des Usines Chimiques Rhone-Poulenc, E. P. 318970; abst. J. S. C. I. 1931, **50**, 242-B. Compare E. P. 302115.

2. Society of Chemical Industry in Basle, E. P. 318255; abst. C. A. 1930, **24**, 2291; J. S. C. I. 1931, **50**, 108-B. In Swiss P. 145054; Addn. to Swiss P. 142175; abst. C. A. 1931, **25**, 2288, 5287, they describe a new cellulose derivative obtained by the action of alkali-cellulose and aniline on cyanuric chloride.

3. Societe pour la Fabrication de La Soie "Rhodiaseta," E. P. 313072; abst. C. A. 1930, **24**, 977; J. S. C. I. 1930, **49**, 1107-B; Silk J. 1929, **6**, #64, 68. F. P. 655435; abst. C. A. 1929, **23**, 4071.



dine, *p*-chloraniline, and 5-chlor-*o*-toluidine<sup>1</sup>. Spicers, Ltd.<sup>2</sup>, have described an apparatus for the casting of thin films of cellulose ethers, and have devised a method of treating sheets and films of the same<sup>3</sup>, comprising passing the sheet, after it leaves the surface on which it is formed, through an electrically conducting aqueous bath (as 0.5-1. % NaOH) capable of wetting the sheet or film, the bath being electrically connected to earth.

In the glueing of leather<sup>4</sup>, the surfaces to be affixed are first moistened with a solvent for the adhesive material consisting of finely powdered, dry cellulose ether or ester, and the surfaces joined by combined heat and pressure. In coating compositions containing rubber<sup>5</sup>, and claimed as especially suitable for use on metal, wood, leather and cloth, the rubber is mixed with a drying oil, ethylcellulose, and a dryer as cobalt linoleate, which acts as a mutual catalyst for the curing of the rubber and thickening of the oil. In preparing chloracetic anhydride<sup>6</sup>, chloracetyl chloride is heated with monochloracetic acid in the presence of aluminum chloride.

C. Trogus and K. Hess<sup>7</sup> in X-ray studies with cellulose derivatives, have determined the translation lattice of fibrous methylcellulose and found,  $a = 21.3$  A.U,  $b = 25.6$  A. U. and  $c = 11.3$  A. U. Cellulose ethers insoluble in all simple

1. E. Speight, U. S. P. 1780320; abst. C. A. 1931, **25**, 1101; J. S. C. I. 1930, **49**, 1149-B. E. P. 314651; abst. C. A. 1930, **24**, 1522; J. S. C. I. 1929, **48**, 716-B. Cites E. P. 2718, 1892.

2. Spicers, Ltd., D. R. P. 487646; abst. C. A. 1930, **24**, 1979.

3. Spicers, Ltd., Can. P. 291437.

4. W. Stelkens, E. P. 314867; abst. J. S. C. I. 1930, **49**, 1081-B; Brit. Plastics, 1930, **2**, #19, 132.

5. C. Stine and C. Coolidge, U. S. P. 1728632; abst. C. A. 1929, **23**, 4583; J. S. C. I. 1929, **48**, 826-B. See U. S. P. 1663100, 1663101, 1700778, 1700779.

6. C. Strosacker and C. Schwegler, U. S. P. 1713104; abst. C. A. 1929, **23**, 3234; J. S. C. I. 1929, **48**, 887-B; Chem. Zentr. 1929, II, 1215.

7. Z. physik. Chem., 1929, **4**, #5, 321; abst. C. A. 1930, **24**, 2287; J. S. C. I. 1929, **48**, 1222-A; Chem. Zentr. 1929, II, 1912.

solvents<sup>1</sup>, are obtained by treating alkal cellulose with alkyl halide in the presence of water but in the absence of any added salt. The manufacture of ethylcellulose soluble in mixed solvents and using ethyl chloride is described. Dyes are obtained by condensing *p*-aminodiphenylamine or 4-aminodiphenylamine-4'-methyl-2-sulfonic acid with a di-nitrohaloaryl compound. These dyes give fast yellow to reddish brown tints on cellulose ethers and esters<sup>2</sup>. In preparing composite or built-up sheets<sup>3</sup>, layers of material which swell in water as the cellulose ethers are joined with layers of celluloid which is resistant to water, using an agglutinant also water resistant.

F. Wood<sup>4</sup> has described a cellulose methylene ether (methylenecellulose) obtained by reacting upon alkal cellulose with *s*-dichlorodimethyl sulfate. Other methylene inorganic and organic esters give somewhat similar results. Monochlorodimethyl sulfate forms a mixed methylmethylenecellulose. The physical characteristics of benzylcellulose and films formed from it have been detailed<sup>5</sup>. The Engler viscosity of a 2% solution was 30° in comparison with 120° for cellulose nitrate and 55° for cellulose acetate. H. Dreyfus<sup>6</sup> has described an apparatus for the production of cellulose ether filaments, and a method for producing these

1. A. Wacker Gesellschaft für Elektrochemische Industrie, E. P. 306125; abst. C. A. 1929, **23**, 5041; J. S. C. I. 1930, **49**, 900-B; Cellulose, 1930, **1**, #4, 126; Brit. Plastics, 1930, **2**, #17, 230; Silk. J. 1929, **6**, #61, 72; Chem. Zentr. 1929, I, 3161. F. P. 667307; abst. C. A. 1930, **24**, 1216.

2. H. Wagner, U. S. P. 1709292; abst. C. A. 1929, **23**, 2835; Chem. Zentr. 1929, II, 1852. E. P. 279133; abst. C. A. 1928, **22**, 2847; J. S. C. I. 1928, **47**, 516-B; Chem. Zentr. 1928, I, 756. See U. S. P. 1709256.

3. Wolff & Co. Kommandit-Gesellschaft auf Aktien, and R. Weingand, E. P. 304722; abst. C. A. 1929, **23**, 4819; J. S. C. I. 1930, **49**, 268-B; Chem. Zentr. 1929, I, 2719. F. P. 667942; abst. C. A. 1930, **24**, 1508; Cellulose, 1930, **1**, #4, 126.

4. Nature, 1929, **124**, 762; abst. C. A. 1930, **24**, 1214; J. S. C. I. 1929, **48**, 1427-A. See J. Blanksma, Rec. trac. chim. 1929, **48**, 351, 361; abst. C. A. 1929, **23**, 2700. L. Meunier and R. Guyot, compt. rend. 1929, **188**, 506; abst. C. A. 1929, **23**, 8342. K. Fuchs and E. Katscher, Ber. 1927, **60B**, 2288; abst. C. A. 1928, **22**, 382.

5. Farbe und Lack, 1929, #11, 134.

6. F. P. 677461. See F. P. 531816, 561588, 566383, 654062.

filaments by the dry-spinning or evaporative process<sup>1</sup>, in which voluminous or tubular structures are produced by the use of diacetone alcohol as solvent, and forming the filament at a temperature between 70-90°. He prepares artificial threads of methyl-, ethyl- and benzyl-cellulose of tubular character by dissolving in a solvent mixture containing at least two volatile constituents, spinning temperatures being below the boiling point of the higher boiling component, the difference in boiling points between solvents being adjusted to give the desired voluminosity to the filament<sup>2</sup>. In the calendering and ironing of fabrics composed wholly or in part of the cellulose ethers or esters<sup>3</sup> in such a manner that no increase in luster results, the calendering is done at a temperature around 100° only when the fabric is dry.

In the weighting of cellulose ether or ester filaments or fabrics<sup>4</sup>, the usual tin salts may be replaced by sodium or potassium zincates, which also have a direct affinity for dyestuffs. If it is desired to produce hollow filaments<sup>5</sup>, especially by the dry spinning process, there is added to the spinning solution containing a volatile solvent liquid, one or more high boiling plasticizers as acetyl carbinol, acetyl acetone, acetophenone, ethylidene acetone, cyclopentanone, cyclobutanone or diethyl phthalate, the residual plasticizer being afterwards removed by a washing or solvent treatment. Hollow filaments are obtained by spinning solutions in acetone-acetaldehyde at 63°, in acetone-acetaldehyde-alcohol at 70°, in alcohol-methyl formate at 63°, and in acetone-water<sup>6</sup> at just below 100°.

In order to obtain dull luster cellulose ether threads<sup>7</sup>, they are produced by spinning in the dry or wet process

1. E. P. 317097.      2. E. P. 317098.
3. C. Palmer, U. S. P. 1732340.
4. British Celanese, Ltd., and G. Ellis, E. P. 306611; abst. *Silk J.* 1929, **6**, #61, 72.
5. H. Dreyfus, E. P. 317097.
6. *Ibid.* E. P. 317098. See also E. P. 165519, 182166, 198023, 203092, 209125, 210108, 317097.
7. *Ibid.* E. P. 346793; abst. *J. S. C. I.* 1931, **50**, 799-B.

solution of cellulose derivatives containing natural or artificial resins, preferably those melting above 250°. Cellulose ether emulsions<sup>1</sup>, especially the "oil-in-water" type, are obtained by dissolving (say) benzylcellulose in a solvent less volatile than water, the volatility being sufficiently great so that the time of drying of the film is not unduly prolonged and tough transparent films result. Cyclohexanone and tricresyl phosphate answer these conditions. In the preparation of cellulose ester emulsions as those of nitrocellulose<sup>2</sup>, it is advised, especially when pigments are incorporated, to use water-soluble ethers as methylcellulose, sold as Colloresin "D."

To prepare benzylcellulose of an unusually high degree of benzylation<sup>3</sup>, and especially suitable for lacquer, enamel and film formation, cellulose is mercerized with 18-20% NaOH solution for 1-2 hours, pressed until the mass weighs 2.5 times the weight of the original cellulose (which requires a very high degree of pressure), shredding, maturing at 25° for 60-90 hours, and then mixed with 50 parts powdered NaOH and 150 parts benzyl chloride. The mixture is heated for 8 hours, stirring continuously meanwhile, keeping the temperature at 95-110°. A further addition of 150 of benzyl chloride is made and heat continued 16 hours. The crude ether may be extracted with denatured alcohol, precipitated in water and washed to neutrality.

**Progress Chronicled In 1930.** In the year 1930 appeared a greater variety of investigations, methods of preparation and industrial applications suggested, than in any previous year, as indicated by the following abbreviated resume.

1. G. Davies, W. Jenkins and Imperial Chemical Industries, Ltd., Australia P. 23003, 1929.

2. *Ibid.* Australia P. 23004, 1929. Cites E. P. 274611.

3. D. Traill and Imperial Chemical Industries, Ltd., Australia P. 23156, 1929.

In order to reduce the electrical discharge of fibers, especially those containing cellulose ethers and esters<sup>1</sup>, the fibers are impregnated with a mixture of oils or fats and fatty acids to which is added an organic base forming an oil-soluble soap (butylamine, dibutylamine, piperidine, "sapa-mines," mono-, di- and tri-ethanolamine, aminoethylamine oleate). In the manufacture of artificial silk and films from cellulose ethers with the use of an aqueous precipitating bath<sup>2</sup>, the bath is covered with a layer of liquid which is immiscible or but partially miscible with the constituents of the bath but dissolves the solvent used in preparing the cellulose derivative, fatty oils or the higher fatty acids being suitable.

Benzene-soluble ethylcellulose has been brought forward as a useful undercoat of airplane wing fabric<sup>3</sup>, a suitable formula being ethylcellulose 12, benzyl alcohol 2, methyl alcohol 13, benzene 60. For producing a floor or wall covering<sup>4</sup>, benzylcellulose 20 is mixed with tricresyl phosphate 27, with fillers (wood meal or China clay) and dyes, then pressed onto jute. Peat has been brought forward as a useful cellulosic material for etherification and esterification purposes<sup>5</sup>, the peat being treated under pressure with ammonia, acidifying and washing to neutralization. An alkali is then added and finally etherifying.

In the production of ornamental effects on fabrics<sup>6</sup>, "seersucker" (crinkled or puckered) fabric comprising cellulose ether or ester silk, is produced by printing or spray-

1. Aceta, G. m. b. H., E. P. 346912; abst. J. S. C. I. 1931, **50**, 626-B; F. P. 689984; abst. C. A. 1931, **25**, 1103.

2. *Ibid.* D. R. P. 505332; abst. C. A. 1930, **24**, 6015. See U. S. P. 1599230, 1634980.

3. T. Araki and T. Nagamote, J. S. C. I. (Japan) 1930, **33**, 382-B; abst. C. A. 1931, **25**, 1398; Cellulose, 1930, **1**, 292; J. S. C. I. 1931, **50**, 502-B.

4. H. Boernstein and N. V. Nederlandsche Linoleum Fabrik, Dutch P. 21183; abst. C. A. 1930, **24**, 2857.

5. A. Bosse, E. P. 337360; abst. C. A. 1931, **25**, 2290. F. P. 677479; abst. C. A. 1930, **24**, 3113.

6. British Celanese, Ltd., E. P. 335138; abst. J. S. C. I. 1930, **49**, 1106-B. See E. P. 274584; abst. J. S. C. I. 1927, **46**, 747.

ing woven or knitted materials with a solution of nitric acid (sp. gr. 1.03-1.30), allowing it to react for 1-10 minutes and then washing. Shrinkage of the treated parts causes puckering of the non-treated parts of the fabric. A material suitable for raincoats or bathing-suit bags comprises a fabric base having on it a layer of rubber composition and also a layer of cellulose ether or ester together with a compatible synthetic resin<sup>1</sup>. An apparatus for making cellulose ether filaments by extrusion<sup>2</sup>, comprises a spinning cell in which an evaporative medium flows counter-current to the filaments, additional evaporative medium being introduced near the jet.

In mordanting, weighting and dyeing<sup>2</sup>, films and textile materials are treated with a high-speed stream of metal oxide or of oxidizable metal, the metal on the fabric being subsequently oxidized, whereby the oxide so thoroughly impregnates the material that mordant dyeing is rendered possible. The process is claimed as particularly suitable for treating cellulose ether and ester materials, and is conveniently carried out by means of the Schoop metallising apparatus. Suitable metals include zinc, aluminum, tin and their alloys. Filaments and threads of cellulose derivatives with water-soluble salts as ammonium thiocyanate or zinc chloride<sup>4</sup>, are freed from the soluble salts without loss of luster by effecting the washing, bleaching and dyeing treatments in the presence of luster-preserving or relustering substances (sodium chloride, sodium acetate, ammonium chloride, potassium or ammonium sulfates, diethyl tartrate, ethyl lactate, diacetone alcohol, acetin).

1. British Celanese, Ltd., E. P. 338065; abst. C. A. 1931, **25**, 2305.

2. British Celanese, Ltd., J. Briggs and R. Roberts, E. P. 325233; abst. C. A. 1930, **24**, 4156. See E. P. 203092, 300998, 304674.

3. British Celanese, Ltd., W. Dickie and F. Hill, E. P. 337813; abst. C. A. 1931, **25**, 2304; J. S. C. I. 1931, **50**, 197-B. See E. P. 314208.

4. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 328911; abst. C. A. 1930, **24**, 5512; J. S. C. I. 1930, **49**, 761-B. See E. P. 246879, 259265, 259266; abst. J. S. C. I. 1926, **45**, 317, 976, 1008.

Filaments of the cellular or tubular type are obtained by leading a cellulose ether or ester into a cell or chamber<sup>1</sup> through which passes a current of an evaporative medium, and films of increased strength<sup>2</sup>, the filaments after extrusion dies. In producing cellulose ether or ester filaments and films of increased strength<sup>14</sup>, the filaments after extrusion are met with a counter-current of evaporating medium in the spinning cell, by applying a uniform controlled stretch where the product still contains residual solvent and is in a semi-solid or plastic condition (preferably while containing 20-40% solvent).

In the waterproofing of materials containing cellulose ethers<sup>3</sup>, insoluble metal soaps may be introduced by treating the cellulose ether with a swelling agent and a soluble metal salt (chloride, sulfate or thiocyanate of tin, aluminum, iron or chromium). The swelling agents applicable include lactic acid, diacetin, phenol, urethanes, thiourethanes or guanidine. The treated material is subsequently brought into contact with solutions of soluble soaps. The resulting products have a subdued luster and improved resistance to water. Cellulose ether and ester silk may be dyed with (preferably unsulfonated) azo dyes derived from nitroarylamines containing two or more linked aryl residues. Examples, 2,4-dinitro-4'-aminodiphenylamine with phenol (yellow), 3-nitro-4-diaminodiphenyl ether with *a*-naphthylamine (bluish-red), 2,2'-dinitrobenzidine with 2 mols. *m*-toluidine (orange), 4-nitro-4'-aminodiphenyl with *m*-phenylenediamine (orange-brown), 5-nitro-*o*-toluidine with 2 mols. *a*-naphthylamine or with 2 mols. 2,3-dihydroxynaphthoic acid (black),

1. British Celanese, Ltd., H. Dreyfus and R. Roberts, E. P. 324899; abst. C. A. 1930, **24**, 3901. Cf. E. P. 300998; abst. C. A. 1929, **23**, 4072. E. P. 317097, 317098.

2. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 331229; abst. C. A. 1931, **25**, 204. Cf. E. P. 323790, 329620.

3. British Celanese, Ltd., and G. Ellis, E. P. 323501; abst. C. A. 1930, **24**, 3119; J. S. C. I. 1930, **49**, 281-B.

and 3,3'-dinitro-4,4'-diaminodiphenylmethane with 2 mols. *m*-tolylenediamine (golden-brown)<sup>1</sup>.

In the weighting and mordanting of textile materials containing cellulose ethers<sup>2</sup>, insoluble metal compounds of tin, iron, aluminum or chromium are fixed on the material by successive application without intermediate washing, but applied in such limited quantity that all is retained. To improve the resistance to delustering with substantially dry steam<sup>3</sup>, products comprising cellulose ethers and esters are incorporated during or after their production with a solvent or gelling agent. The cellulose ether may have its luster restored (relustered)<sup>4</sup> or are protected from the action of delustering agents such as hot aqueous media by treatment with substantially dry steam.

Cellulose ethers or esters may be waterproofed by treatment with an emulsion of wax in a soap solution, the soap being precipitated in the material in the form of an insoluble metallic soap, the acetates or chlorides of tin, aluminum, calcium, iron, barium, chromium, zinc or antimony being used as precipitating agents<sup>5</sup>. The metal radical is applied while the cellulose derivative is in a swollen condition. In producing discharge effects applicable to the cellulose ethers<sup>6</sup>, textiles are impregnated with a substance of acid reaction prior to the application of the discharging agent for a coloring matter, and discharge being effected in the presence of the acid substance, which may be oxalic, tartaric, citric, salicylic, benzoic or naphthoic acids, a sulfonic or benzenesulfonic acid of phenol, naphthalene or

1. British Celanese, Ltd., E. P. 323792; abst. J. S. C. I. 1930, **49**, 370-B; C. A. 1930, **24**, 3382. In this connection see E. P. 222001, 237943, 239470, 283253, 283081, 310779.

2. *Ibid.* E. P. 329659; abst. C. A. 1930, **24**, 6034. Cf. E. P. 258874, 260290, 273693, 280698, 285941.

3. *Ibid.* E. P. 332187; abst. C. A. 1931, **25**, 205; J. S. C. I. 1930, **49**, 944-B. See R. Clavel, E. P. 269605.

4. *Ibid.* E. P. 332231; abst. C. A. 1931, **25**, 218; J. S. C. I. 1930, **49**, 944-B.

5. *Ibid.* E. P. 323785, Addn. to E. P. 323501; abst. C. A. 1930, **24**, 3368; Cellulose, 1930, **1**, 198.

6. *Ibid.* E. P. 334518; abst. C. A. 1931, **25**, 1100. See E. P. 324650.



naphthol, or an acid salt as aluminum or zinc sulfates. In another method<sup>1</sup>, in addition to chlorates, chromates may be used as discharging agents. For colored discharges a nitrodiarylamine, aminoanthraquinone, or acylaminoanthraquinone is added to the discharge paste.

Luster-preserving treatments on cellulose ether or ester textiles<sup>2</sup> may be utilized in the production of printed luster patterns. The cellulose ether textile<sup>3</sup> may be dyed with oxidation Aniline Black in the presence of considerably greater proportions of acid than those commonly used in the dyeing of cotton materials; the excess of acid being in the form of a mineral acid or acid salt, but preferably an organic acid. Cellulose ether or ester fabrics may be embossed and effect materials applied locally by a roller making contact with only the raised portions of the fabric; e.g., the fabric is treated with a solution of sodium *p*-cresolate to which is added Caledon Jade green paste and sodium hydrosulfite powder, then with an oxidizing solution containing olive oil soap and sodium perborate; finally with 1-amino-2-methylanthraquinone and 1-methylamino-4-hydroxyanthraquinone<sup>4</sup>.

Ethers or esters of cellulose may be dyed with azo dyes containing an *ar*-tetrahydronaphthyl group, preferably having no sulfonic group. Examples, *ar*-tetrahydro-*b*-naphthylamine with phenol (yellow), 2,3-hydroxynaphthoic-*m*-nitroanilide (orange), *p*-nitroaniline with *ar*-tetrahydro-*a*- or *b*-naphthylamine (orange or golden yellow), *m*-nitroaniline-*ar*-tetrahydro-*a*-naphthylamine (marigold); *p*-nitroaniline-

1. British Celanese, Ltd., E. P. 334543; Addn. to E. P. 312655; C. A. 1931, **25**, 1102; J. S. C. I. 1930, **49**, 1147-B.

2. *Ibid.* E. P. 335583; Addn. to E. P. 332231; abst. C. A. 1931, **25**, 1687; J. S. C. I. 1930, **49**, 1147-B. See E. P. 332187.

3. British Celanese, Ltd., G. Ellis and W. Miller, E. P. 332624; abst. C. A. 1931, **25**, 420; J. S. C. I. 1930, **49**, 1024-B. Cf. E. P. 244143, 324683.

4. British Celanese, Ltd., and R. Felgate, E. P. 323210; abst. C. A. 1930, **24**, 3119; Silk J. and Rayon World, 1930, **6**, #70, 64. See C. Dreyfus, E. P. 254354.

*o*-sulfonic acid with *ar*-tetrahydro-*a*-naphthylamine (orange-red)<sup>1</sup>.

*N*-Nitroaryl-*ar*-tetrahydro-naphthylamines are suitable for dyeing the cellulose ethers and esters<sup>2</sup>, and are made by condensing *ar*-tetrahydronaphthylamines or a derivative with nitrated aromatic compounds containing one or more labile halogen atoms such as 2-nitro-, or 2,4-dinitro-chlorbenzene, 2-nitrobrombenzene, 2,5-dichloronitrobenzene, 2,4-dinitrochlorbenzene-6-sulfonic acid or -6-carboxylic acid. The insoluble dyes may be applied in suspensions or dispersions.

In order to produce artificial filaments in masses suitable for spinning and weaving operations (i.e., staple fiber)<sup>3</sup>, the filaments are subjected to a fluid blast, stream or jet so as to produce a tangled mass which may then be used in spinning operations. In another method<sup>4</sup>, a number of filaments extruded from a plurality of spinning orifices are associated and physically united to form a single larger filament, the fluid stream of cellulose derivative being extruded into a medium rich in the solvent employed, so that they converge together while in a tacky condition to produce a unitary filament of relatively large cross-section<sup>5</sup>. Or the large filament may be formed from twisted or untwisted bundles of filaments<sup>6</sup>, by moistening them with a swelling agent so that the individual filaments coalesce. The unitary filament may contain different types of yarns or even metallic wires.

1. British Celanese, Ltd., and H. Olpin, E. P. 330591; abst. C. A. 1930, **24**, 6033; J. S. C. I. 1930, **49**, 902-B. See E. P. 219349, 224925, 242393, 242711, 269960, 273819, 273820, 322737, 323788.

2. *Ibid.* E. P. 330602; abst. C. A. 1930, **24**, 6032.

3. British Celanese, Ltd., and W. Taylor, E. P. 323221; abst. Silk J. and Rayon World, 1930, **6**, #70, 64. See E. P. 165519, 198023, 322557, 323209.

4. *Ibid.* E. P. 326461; abst. C. A. 1930, **24**, 4931; J. S. C. I. 1930, **49**, 504-B.

5. *Ibid.* E. P. 326462; abst. C. A. 1930, **24**, 4931; J. S. C. I. 1930, **49**, 553-B.

6. *Ibid.* E. P. 327740; abst. C. A. 1930, **24**, 5169.

A luster-modifying liquid may be applied to cellulose ether or ester filaments<sup>1</sup> while they still contain a relatively large proportion of solvent. Water, gasoline and paraffin reduce luster; toluene and xylene enhance it. All types of artificial filaments are delustered to any desired degree by subjection to a process of abrasion in which the threads are led over abrasive surfaces or over loose abrasive material. Solid abrasives include kieselguhr, pumice, powdered glass, carborundum and emery. Other abrasives which are soluble in solvents and can thus be completely removed from the delustered threads include sodium sulfate, alum and sodium chloride.

Artificial silk yarns composed of the ethers or esters of cellulose<sup>2</sup> may be colored intermittently with fast dyes at regular or irregular spaced intervals along their length by means of suitable devices which rotate or oscillate, or reciprocate in contact with the traveling yarn. Intermittently colored, multi-colored or cross-dyed effects on subsequent dyeing result by applying a saponifying agent at intervals along the length of the material while it is in motion<sup>3</sup>, preferably continuously with production, for which purpose various alkali solutions may be used.

Cellulose ethers and esters of relatively low luster<sup>4</sup> are made by extruding solutions into a volatile solvent (acetone), or a mixture of a volatile solvent and a diluent (water) into an evaporative medium which is at a higher temperature than the spinning solution, the latter being maintained at 10-20° below the minimum temperature required for producing a product of normal high gloss. In

1. British Celanese, Ltd., E. P. 328247; abst. C. A. 1930, **24**, 5512; J. S. C. I. 1930, **49**, 763-B.

2. *Ibid.* E. P. 332565; Addn. to E. P. 332263; abst. C. A. 1931, **25**, 421; J. S. C. I. 1930, **49**, 1063-B. See E. P. 325823.

3. *Ibid.* E. P. 332263; abst. C. A. 1931, **25**, 217.

4. British Celanese, Ltd., W. Taylor and R. Roberts, E. P. 334195; abst. C. A. 1931, **25**, 1084; J. S. C. I. 1930, **49**, 1023-B. See E. P. 320632; abst. J. S. C. I. 1930, **49**, 53. E. P. 315729, 198023, 333504.

the fabrication of threads of relatively low luster<sup>1</sup>, the temperature of the spinning solution and that of the evaporative medium are separately controlled. Reduced luster may also be obtained<sup>2</sup> in the dry-spinning of cellulose ether and ester solutions by the use of a water-soluble barium salt (nitrate, acetate or chloride) and subsequently treating the formed filaments with a fixing solution of soluble sulfate or phosphate to produce barium sulfate or phosphate.

Fabrics of cellulose derivatives<sup>3</sup> are capable of reproducing fine distinctions of light and shade when printed with plates or rollers engraved to a large number of gradations of depth, the plate or roller then furnished with various colors<sup>4</sup>. Pentaerythrite ethers have been produced<sup>5</sup> of value as solvents and softeners for cellulose ethers. Pentaerythrite is etherified with ethyl (methyl, propyl, butyl, benzyl) chloride and sodium hydroxide in benzene, to give mono-, di- and tri-ethers, monomethylerythritol being an example. A coating composition has been devised<sup>6</sup>, which consists in mixing deaggregated rubber with ethylcellulose, perilla oil, cobalt linoleate and a softener.

S. Carroll<sup>7</sup> has delineated the preparation of a cellulose ether film especially applicable to photography, comprising colloiddized ethylcellulose with a mono- or poly-brom naphthalene or anthracene, *α*-bromnaphthalene being pre-

1. British Celanese, Ltd., E. P. 334198; Addn. to E. P. 334195; abst. C. A. 1931, **25**, 1084; J. S. C. I. 1930, **49**, 1023-B. See E. P. 300998, 320363.

2. British Celanese, Ltd., W. Taylor, R. Roberts and L. Gregory, E. P. 334563; abst. C. A. 1931, **25**, 1084; J. S. C. I. 1930, **49**, 1063-B. Cf. E. P. 259899, 279502, 281084, 284798, 329659, 273692, 273693, 280698, 285948, 286761, 287204, 328247, 333504.

3. British Celanese, Ltd., and J. Wainwright, E. P. 335206; abst. C. A. 1931, **25**, 1391; J. S. C. I. 1931, **50**, 17-B.

4. Such colors as those described in E. P. 219349, 220505, 224681, 224925, 227183, 237943, 239470, 242393, 242711, 253978, 263260, 269960, 273819, 273820, 283081, 283253, 298993, 299343, 299349, 300929, 305560, 306981, 310827, 311433, 316526, 319390, 327860, 321401, 322737, 323788, 323792, 330591, 330602.

5. C. Burke, U. S. P. 1774500; abst. J. S. C. I. 1931, **50**, 621-B.

6. Canadian Industries, Ltd., Can. P. 806541.

7. U. S. P. 1763035; abst. *Plastics*, 1930, **6**, 457. In this connection see L. Lilienfeld, U. S. P. 1188376. W. Webb, U. S. P. 1583709.

ferred. Solutions and plastic masses are prepared from cellulose ethers by incorporating with them partially or wholly polymerized vinyl compounds (vinyl acetate, propionate, phthalate, chloride, bromide), or styrene (vinylbenzene) together with solvents<sup>1</sup>. Thin bands are formed comprising two continuous layers such as ethyl- or benzyl-cellulose or cellulose acetate<sup>2</sup>, one layer containing a material as powdered magnesia or lithopone to enhance its affinity for adhesives.

R. Clavel<sup>3</sup> prepares artificial leather by treating textiles with cellulose ether or ester in solution, followed by a tannin bath and treatment with bismuth nitrate solution. Cellulose ether-esters have been described<sup>4</sup>, prepared by treating alkalicellulose with a relatively small amount of ethyl sulfate at 25°, the free alkali removed and the product dried, acetylated and subjected to a partial hydration treatment. The ethylcellulose acetate contains not more than one ethyl group to each C<sub>6</sub> cellulose group (about 13.5% ethyl). To avoid the high cost of the vehicle in the production of cellulose ether and ester enamels, emulsions of the latter of the water-in-oil type which give tough and transparent films, may be prepared by dispersing water to an extent such that it is substantially absorbed in the emulsion, in a solution of the ether or ester in a solvent (cyclohexanone, methylcyclohexanone) which is only slightly miscible with water<sup>5</sup>. Aqueous emulsions may also be prepared<sup>6</sup>, applicable as spraying enamels, by dispersing in

1. Celluloid Corp., E. P. 335582, Division of E. P. 308658; abst. C. A. 1930, **24**, 499; J. S. C. I. 1930, **49**, 1146-B; Br. Plastics, 1931, **2**, 376.

2. Chem. Fabr. von Heyden, A. G., E. P. 337501; abst. C. A. 1931, **25**, 2311.

3. D. R. P. 509400; abst. Chem. Ind. 1931, **25**, 958.

4. Courtaulds, Ltd., D. R. P. 514892; abst. C. A. 1931, **25**, 2288.

5. G. Davies, W. Jenkins and Imperial Chemical Industries, Ltd., E. P. 328657; abst. C. A. 1930, **24**, 5517; J. S. C. I. 1930, **49**, 655-B; Br. Plastics, 1930, **2**, #15, 75. F. P. 679440; abst. C. A. 1930, **24**, 3901. Can. P. 314397.

6. *Ibid.* E. P. 328934; abst. C. A. 1930, **24**, 5517; J. S. C. I. 1930, **49**, 760-B; Br. Plastics, 1930, **2**, #17, 101. Can. P. 314396.

water in a colloid mill with the aid of an emulsifying agent a cellulose ether or ester as above.

In stencil manufacture<sup>1</sup>, benzyl-, *p*-chlorbenzyl- and phenylethyl-celluloses are dissolved in a volatile solvent, a plastifier (tetra- or hexa-chloronaphthalene, benzoylbutyl tartrate) added, and applied to Yoshino paper. The isolation of benzylcellulose from a crude reaction mixture is effected by admixture with sodium chloride, followed by extraction with benzene and removal of residual salt by washing with water. The viscosity of methyl-, ethyl- and benzyl-cellulose<sup>3</sup>, may be changed within wide limits by modifying the percentage of plastifying agent (tricresyl phosphate, diethyl phthalate, dibutyl tartrate) in respect to the volatile solvent portion (acetone, methylethyl ketone, benzene, chloroform). C. Dreyfus<sup>4</sup> has described ethyl-cellulose coating compositions of viscosity below 5 (Ostwald viscosimeter) and preferably between 0.1-5.

In the preparation of solutions of organic derivatives of cellulose for artificial filament formation<sup>5</sup>, the solvent comprises a volatile liquid with ethylene glycol, diethylene glycol or ethylene glycol monomethyl ether. In the manufacture of cellulose ethers directly<sup>6</sup>, the cellulose material is treated with an etherifying agent as ethyl sulfate and a small amount of alkali as sodium carbonate or hydroxide, afterwards adding an alkali to the mixture and allowing the materials to react. An enamel has been patented<sup>7</sup> comprising a cellulose ether (benzylcellulose) with a synthetic resin and volatile solvents. If filaments of methyl-, ethyl- or benzyl-cellulose are treated while under tension with concentrated mineral acids for a short time (from a

1. A. Davis, U. S. P. 1771165; abst. C. A. 1930, **24**, 4598; J. S. C. I. 1931, **50**, 344-B.

2. E. Doerr, U. S. P. 1751685; abst. C. A. 1930, **24**, 2599; Cellulose, 1930, **1**, 150.

3. C. Dreyfus, F. P. 673029; abst. C. A. 1930, **24**, 2292; Kunst. 1931, **21**, 17.

4. F. P. 673030; abst. C. A. 1930, **24**, 2316.

5. *Ibid.* F. P. 676728; abst. C. A. 1930, **24**, 3113.

6. *Ibid.* F. P. 677927; abst. C. A. 1930, **24**, 3368.

7. *Ibid.* Can. P. 302649.

half second up) the tensile strength is said to be increased<sup>1</sup>. Increased tensile strength is also said to result<sup>2</sup> when the filaments are continuously stretched while in the set elastic condition during their travel from one point to another, being simultaneously or previously treated with solvents or swelling agents.

To diminish the water-repelling properties and to facilitate dyeing with direct or mordant dyes on cellulose ether threads<sup>3</sup>, they are impregnated with regenerated cellulose, i.e. viscose, cuprammonium or zinc chloride solutions of cellulose and precipitating in the usual way, or with nitrocellulose followed by denitration. Ethylcellulose or acetocellulose films and ribbons are prepared by using as a solvent medium a non-solvent liquid and volatile solvent in such proportions that they do not form a solvent, then adding one or more high-boiling solvents in sufficient amount to impart dissolving power to the solution as a whole. The reason for this is that it is thus possible to start with an inexpensive solvent combination in which the solvent power is progressively augmented by increase of proportion of high-boiling solvents during the evaporative process<sup>4</sup>.

Cellulose ether and ester films are made to adhere to glass by incorporation of a synthetic resin of the phenol-furfuraldehyde, aniline-furfuraldehyde type, or acaroid resin<sup>5</sup>, and applying heat and pressure. H. Dreyfus<sup>6</sup> reduces the capacity of the hydroxyalkyl celluloses (cellulose hydroxyalkyl ethers) for dissolving or swelling in water by ether-

1. H. Dreyfus, E. P. 324662; abst. C. A. 1930, **24**, 3900; J. S. C. I. 1930, **49**, 319-B.

2. *Ibid.* E. P. 323790; abst. C. A. 1930, **24**, 3369; J. S. C. I. 1930, **49**, 319-B. Compare E. P. 277089.

3. *Ibid.* E. P. 323521; abst. C. A. 1930, **24**, 3112; J. S. C. I. 1930, **49**, 237-B.

4. *Ibid.* E. P. 333926; abst. C. A. 1931, **25**, 815. Cites E. P. 207562, 275286, 320363.

5. *Ibid.* E. P. 326520; abst. C. A. 1930, **24**, 4910; J. S. C. I. 1930, **49**, 558-B. Cf. E. P. 299067, 299782, 307462, 320374.

6. E. P. 327157; abst. C. A. 1930, **24**, 5157; J. S. C. I. 1930, **49**, 610-B. Cf. E. P. 277721.

ifying a portion of the hydroxy groups. Tri(hydroxyethyl)-cellulose may be ethylated to ethoxyethylcellulose.

It is recommended in the formation of filaments or films to use acetone solutions of cellulose ethers or esters containing such a proportion of water (suitably 10-12%) that the viscosity of the solution is substantially reduced, which facilitates production of filaments of fine denier<sup>1</sup>, the process being especially applicable to the dry-spinning method. In the production of mordanted or weighted textiles<sup>2</sup>, cellulose ethers or esters containing fixed metal residues are obtained by spinning an acetone solution containing a soluble metal salt and then treating either directly in the coagulating bath (in wet-spinning) or subsequently with substances capable of precipitating the metal. Suitable salts include stannic or ferric chlorides and thiocyanates, aluminum or chromium thiocyanate or zinc chloride, and as precipitants, tannin, ammonia, disodium phosphate and sodium carbonate.

In the coagulation of products formed from cellulose ethers and esters<sup>3</sup>, they are treated with an "organo-mineral acid" (methyl-, ethylene, 1,2- or 1,3-propanedi-, benzene-, phenol-, sulfonic and disulfonic acids; sulfoacetic sulfosuccinic, sulfosalicylic, sulfophthalic, dimethylphosphinic, or nitrophenylphosphinic acids, or naphthalene- and naphthol-sulfonic acids) of 30-50% concentration as precipitants. Threads and fabrics of the alkyl or acyl celluloses may be increased in tensile strength, extensibility and elasticity<sup>4</sup>, by treatment with neutral solvents in relatively high concentration, to that a superficial filming or actual plasticizing of the material takes place, the treated mater-

1. H. Dreyfus, E. P. 328636; abst. C. A. 1930, **24**, 5496; J. S. C. I. 1930, **49**, 656-B. See E. P. 320363; abst. C. A. 1930, **24**, 2600 F. P. 672306; abst. C. A. 1930, **24**, 2293.

2. *Ibid.* E. P. 336621; abst. C. A. 1931, **25**, 1995; J. S. C. I. 1931, **50**, 197-B. Compare E. P. 259899, 308322, 308323, 309201 312095, 312096.

3. *Ibid.* E. P. 334853; abst. C. A. 1931, **25**, 1379; J. S. C. I. 1930, **49**, 1147-B.

4. *Ibid.* E. P. 336217; abst. C. A. 1931, **25**, 1995; Silk J. 1931 **7**, #80, 54; Chim. et Ind. 1931, **25**, 955.



ials being placed under only sufficient tension to prevent shrinkage.

Textiles containing the cellulose ethers or cellulose acetate are colored with dyes prepared by diazotizing 2,4-dinitro-6-alkoxy (or alkyl) anilines (as 3,5-dinitro-*o*-toluidine, -*o*-anisidine or *o*-phenetidine) and coupling with naphthylamine, oxyethyl-*a*-naphthylamine or oxypropyl-1-naphthylamine<sup>1</sup>. Materials simulating celluloid are producible from methyl-, ethyl- or benzyl-cellulose<sup>2</sup>, by incorporating therewith aromatic acylated amines, acetyl-4-brommethylanilide, acetyl-2,4- (or 3,4) dibromanilide, acetyl-2,4,6 (or 2,4,5)-tribromanilide, diacetyl-2,4,6-tribromanilide, acetyl-2,4,6-tribrommethylanilide, diacetyl-3,5-dibrom-2-toluide, acetyl-1,3,6-tribrom-2-naphthalide and benzoyl-2,4,6-tribromanilide being specified.

Cellulose ethers may be weighted and a scroop imparted to fabrics made from them<sup>3</sup> by the use of soluble salts of tin, aluminum, chromium or iron, which are afterwards rendered insoluble by treatment with fatty acids (formation of insoluble oleates, palmitates and stearates). Tubular artificial silk filaments are obtainable by extruding a solution of cellulose acetate or ethylcellulose into a chamber through which passes a current of evaporative substance, heat being concentrated in the region of the spinning nozzles. The idea is to intumesce the filament during evaporation of solvent therefrom<sup>4</sup>.

In order to obtain fine denier with high tensile strength<sup>5</sup>, acetone solutions of cellulose ethers or esters are used containing such a proportion of water that the viscosity of the solution is substantially reduced as compared

1. H. Dreyfus, F. P. 675465; abst. C. A. 1930, **24**, 2890. Cf. F. P. 666626; abst. C. A. 1930, **24**, 1518.

2. *Ibid.* F. P. 675745; abst. C. A. 1930, **24**, 2881. Cites F. P. 498726; and Addn. 21381 to F. P. 498726.

3. *Ibid.* F. P. 677263; abst. C. A. 1930, **24**, 3119; Nitro-cellulose, 1931, **2**, #4, 87.

4. *Ibid.* F. P. 678400; abst. C. A. 1930, **24**, 3647. Cites F. P. 531816, 561588, 566385, 654062, 666898, 667209.

5. *Ibid.* F. P. 683076; abst. C. A. 1930, **24**, 4632.

with that of a solution in commercial acetone, 10-12% of water being stated as suitable. Cellulose derivatives are prepared by treating cellulose with organic acid esters (methyl, ethyl, amyl, benzyl, *m*- and *p*-xylenyl acetates, ethyl laurate, diethyl oxalate, dimethyl or diethyl malonate or succinate, ethyl ethoxyacetate) and in the presence of organic bases such as alkylpiperidines (methyl or ethyl-piperidine), dimethyl-*n*-hexylamine or isoamyl-diethylamine. The cellulose compounds obtained are said to be readily dissolvable and capable of producing tough films<sup>1</sup>.

Threads and filaments of increased strength of cellulose ether and ester<sup>2</sup> are obtained by applying to the threads, while passing through the spinning cell, a counter-current of evaporative medium to produce a controlled uniform stretch at a predetermined part of the threads which still contain residual solvent and is in a semi-solid or plastic condition (i.e. stretch spinning). The threads are stretched by passing them around a roller to which an adjustable drag or braking action is applied<sup>3</sup>, and which is rotated by a stress of the threads. An apparatus has been devised to apply glue or other dressing agent to the filaments<sup>4</sup>. An improvement on the process has been patented<sup>5</sup> comprising a line of extrusion nozzles and a collector device.

In dyeing cellulose ethers and esters black<sup>6</sup>, an aromatic amine is oxidized on the material in the presence of a small amount of mineral acid chemically equivalent to this amine, and in the presence of an acid salt. Example, aniline in the presence of hydrochloric acid and acetic acid is oxidized with a chlorate to give a deep black. In order to impart a subdued luster to products containing cellulose

1. H. Dreyfus, F. P. 685333; abst. C. A. 1930, **24**, 6013. Cf. E. P. 187634. F. P. 629099, 674377.

2. *Ibid.* F. P. 685977; abst. C. A. 1930, **24**, 6015.

3. *Ibid.* F. P. 685978; abst. C. A. 1930, **24**, 6015.

4. *Ibid.* F. P. 685979; abst. C. A. 1930, **24**, 6015.

5. *Ibid.* F. P. 685980; abst. C. A. 1930, **24**, 6015. Compare F. P. 661810, 681317, 681529, 681759; abst. C. A. 1930, **24**, 4392.

6. *Ibid.* F. P. 688755; abst. C. A. 1931, **25**, 1101.

esters or ethers<sup>1</sup> a non-colloidal metallic compound is formed by the reaction of a precipitating agent on a soluble metallic compound, the cellulose material being preferably in the swollen condition. The precipitation of barium sulfate or phosphate or lead sulfate is given as illustrative. Another method of obtaining low luster<sup>2</sup> in artificial threads is by keeping the spinning solution at about 10-20° below the minimum required for the manufacture of products of normal luster.

Textile materials composed of or containing cellulose ethers<sup>3</sup>, are capable of absorbing the desired amount of weighting agent by treatment with acetic or formic acids, the latter inducing the effect of causing a gelling of the fibers. This operation takes place before treatment with tin (aluminum, chromium, iron, zinc, tungsten, bismuth) chloride solution, which is afterwards fixed in a sodium phosphate bath. The weighted materials show an enhanced affinity for dyestuffs. In the manufacture of ribbons<sup>4</sup>, solutions of cellulose ethers in organic solvents miscible with water are passed through narrow slits into a coagulating bath of acid salts or mineral acids. It is claimed that the properties of products of the cellulose ethers which have been coagulated with aqueous agents are improved by the action of heat<sup>5</sup>, which takes place in the presence of the solvents.

A method has been proposed for dyeing material composed of cellulose ether having the novel feature of first loading the material with a water-insoluble metallic compound, and then dyeing the loaded material<sup>6</sup>. It is claimed

1. H. Dreyfus, F. P. 689800; abst. C. A. 1931, **25**, 1103. Compare E. P. 259899, 279502, 286761, 300894. F. P. 621316, 634165 and Addn. 34391 to 634165, 636057, 636058, 642331, 643323, 644565, 644937. See also U. S. P. 1622368.

2. *Ibid.* F. P. 690432; abst. C. A. 1931, **25**, 1084. Cites Addn. 25702 to F. P. 531816, 677461.

3. *Ibid.* F. P. 694881; abst. C. A. 1931, **25**, 1993. Compare Addn. 36175 to F. P. 660623.

4. *Ibid.* F. P. 695843; abst. C. A. 1931, **25**, 2850.

5. *Ibid.* F. P. 695844; abst. C. A. 1931, **25**, 2862.

6. *Ibid.* Can. P. 297692.

that useful additions to cellulose derivatives in the dissolved state for lacquers, varnishes and enamels<sup>1</sup>, are zinc, cobalt, copper and iron-*n*-butyl phthalates. Aliphatic and aromatic cellulose ether solutions are prepared with a solvent comprising methylene chloride alone, or mixed with ethyl alcohol or ethylene chloride<sup>2</sup>.

E. Fischer<sup>3</sup> has worked out the proportional solubilities of varnish ingredients and finds that ethylcellulose and benzylcellulose are insoluble in benzine, nitromethane and acetonitril, but soluble in benzene, cumene, chloroform, ethylene chloride, *s*-dichlorethylene, monochlorobenzene, nitrobenzene, aniline, pyridine, benzyl alcohol, anisol and glacial acetic acid. In preparing cellulose ether and ester composite films<sup>4</sup>, the first layer is made so thin (suitably about 0.01 mm.) as to require a very short time for drying, and after being stripped from its support is used as a carrier band for additional layers.

K. Freudenberg and co-workers<sup>5</sup> have given details of the products obtained by the methylation of cellobiose and similar bodies, and have described heptamethyl-*b*-methylcellobioside, 2,3,6-trimethyl-*b*-methylglucoside, tetramethylglucose 1-chlorhydrin, heptamethyl-*b*-methylmaltoside, heptamethylbenzylcellobioside and decamethyl-*b*-methylcello-trioside, mainly of theoretical interest. They also have prepared methyllignin, nitromethyllignin and brommethyllignin<sup>6</sup>, and in their investigations on the hydrolysis of poly-

1. E. I. du Pont de Nemours & Co., *Farbe und Lack*, 1930, 585; abst. *Nitrocellulose*, 1931, **2**, #1, 17.

2. A. Eichengrün, D. R. P. 508153; abst. C. A. 1931, **25**, 813; *Kunst*, 1931, **21**, 45. Cites E. P. 20975, 1911. Aust. P. 73001.

3. *Farbe und Lack*, 1930, #30, 350; abst. C. A. 1930, **24**, 4646.

4. G. Frenkel, E. P. 332255; abst. C. A. 1931, **25**, 204. Cites E. P. 332254.

5. K. Freudenberg, C. Andersen, Y. Go, K. Friedrich and N. Richtmayer, *Ber.* 1930, **63B**, 1961; abst. C. A. 1931, **25**, 85; J. S. C. I. 1930, **24**, 1412-A.

6. K. Freudenberg and W. Dürr, *Ber.* 1930, **63B**, 2713; abst. C. A. 1931, **25**, 1497; J. S. C. I. 1931, **50**, 74-A; *Z. Angew. Chem.* 1929, **42**, 618.

saccharides<sup>1</sup>, studied various hydrolytic products of the above<sup>2</sup>.

A cellulose trisulfonate is obtained by the action of chlorosulfonic acid in an excess of pyridine on cellulose. Direct exchange of sulfonic groups of the original ester with methyl could not be made. By hydrolyzing with hydrochloric acid in methyl alcohol the ester was decomposed and the regenerated cellulose then was alkylated to a trimethyl-cellulose<sup>3</sup>, nine successive methylations giving an ether of 43% methoxyl, practically insoluble in water.

In the production of multi-color screens for cinematographic films<sup>4</sup>, the film is first dyed, a resist pattern applied and the parts unprotected by the resist bleached and re-dyed. The original film is of alkyl or acyl cellulose. Paper tubes for shotgun cartridges may be waterproofed by coating with a mixture of cellulose ethers or esters<sup>5</sup>, in combination with a resin or ester-gum. Diethylaminoethylcellulose and the corresponding methyl and propyl ether may be prepared<sup>6</sup>, by causing alkal cellulose to be reacted upon with an aliphatic haloalkylamine (chlorethylamine, chlorpropylamine, chlorethylethylaniline, chlorethyldiethylamine).

1. K. Freudenberg and K. Friedrich, *Naturwissenschaften*, 1930, **18**, 1114; abst. C. A. 1931, **25**, 1495.

2. K. Freudenberg, W. Kuhn, W. Dürr, F. Bolz and G. Steinbrunn, Ber. 1930, **63B**, 1510; abst. C. A. 1931, **25**, 1496; J. S. C. I. 1930, **49**, 1025-A. See K. Freudenberg, E. Bruch and H. Rau, Ber. 1929, **62B**, 3078. K. Freudenberg, H. Zocher and W. Dürr, Ber. 1929, **62B**, 1814. K. Freudenberg, W. Belz and C. Niemann, Ber. 1929, **62B**, 1554. K. Freudenberg, Ber. 1929, **62B**, 383. K. Freudenberg, M. Harder, L. Markert and E. Spiess, Ber. 1928, **61B**, 1760. K. Freudenberg, Ann. 1928, **461**, 130.

3. E. Gebauer-Fülneegg and O. Dingler, J. A. C. S. 1930, **52**, 2849; abst. C. A. 1930, **24**, 4149; J. S. C. I. 1930, **49**, 1169-A. See E. Gebauer-Fülneegg, W. Stevens and E. Krug, Monatsh. 1928, **50**, 324. E. Gebauer-Fülneegg, W. Stevens and O. Dingler, Ber. 1928, **61B**, 2000.

4. J. Goldsmith, T. Baker and Spicers, Ltd., E. P. 337073. Refer to E. P. 224571, 257501, 321222, 322432.

5. F. Griffiths, J. Shuffebotham and Imperial Chemical Industries, Ltd., E. P. 327429; abst. C. A. 1930, **24**, 5159.

6. M. Hartmann and Soc. anon. pour l'ind. chim. a Bale, U. S. P. 1777970; abst. C. A. 1931, **25**, 204; *Plastics*, 1931, **7**, #4, 233.

According to W. Haworth *et al*<sup>1</sup>, the acetolysis of trimethylcellulose supports the view that cellobiose is preformed in cellulose. Under mild treatment at low temperatures, fully methylated cellulose undergoes cleavage to a diacetylhexamethylcellobiose which readily gives crystalline heptamethyl-*b*-methylcellobioside. The plastic material of W. Hengstmann<sup>2</sup>, comprises ethyl- or benzyl-cellulose in combination with a natural or artificial resin, rubber and an ester of adipic acid.

In a series of molecular weight determinations in acetic acid, K. Hess<sup>3</sup> found that in very dilute solutions, trimethylcellulose gives too great depressions, increasing markedly with concentration, this effect not appearing to be caused by water in the sample. He has pointed out<sup>4</sup> that the interpretation of X-ray fiber diagrams of trimethylcellulose and cellulose triacetate is attended with grave difficulties, even in respect of the determination of the period of identity along the axis of the fiber, a further complication arising from the possibility that any given fibrous preparation may be a mixture of several forms.

H. Hibbert and L. Marion have studied glycol-lignin, glycol-ether-lignin<sup>5</sup>, and glycol-lignin nitrates<sup>6</sup>, including glycerol-chlorhydrin lignin<sup>7</sup>. A low-esterified cellulose ester (cellulose mon-acetate) or a cellulose mono-ether (mono-ethylcellulose) is used as the starting point in the preparation of cellulose laurate and phenylacetate<sup>8</sup>, the illustra-

1. W. Haworth, E. Hirst and H. Thomas, *Nature*, 1930, **126**, 438; abst. C. A. 1931, **25**, 203; J. S. C. I. 1930, **49**, 1415-A.

2. W. Hengstmann, F. P. 691728; abst. C. A. 1931, **25**, 1345. D. R. P. 499676; abst. C. A. 1931, **25**, 568.

3. K. Hess, *Ber.* 1930, **63B**, 518; abst. C. A. 1930, **24**, 2360; J. S. C. I. 1930, **49**, 456-A.

4. K. Hess and C. Trogus, *Z. physikal. Chem.* 1930, B, **9**, 160; abst. C. A. 1930, **24**, 4929; J. S. C. I. 1930, **49**, 1098-A.

5. *Can. J. Research*, 1930, **2**, 364; abst. J. S. C. I. 1930, **49**, 1275-A.

6. H. Hibbert and L. Marion, *Can. J. Research*, 1930, **3**, 130; abst. J. S. C. I. 1930, **49**, 1418-A.

7. H. Hibbert and J. Phillips, *Can. J. Research*, 1930, **3**, 65; abst. C. A. 1930, **24**, 5757; J. S. C. I. 1930, **49**, 1275-A.

8. I. G. Farbenindustrie, A. G., E. P. 327165; abst. C. A. 1930, **24**, 5043; J. S. C. I. 1930, **49**, 602-B.

tive examples reading upon the formation of such bodies as cellulose aceto-laurate, cellulose acetophenylacetate, ethyl-cellulose laurate and phenylacetate.

A process has been described for the preparation of cellulose ether composition from wood which is treated with an alkylating or aralkylating agent (methyl, benzyl or nitrobenzyl chloride) in the presence of caustic soda<sup>1</sup>, and if desired, conjointly with metal oxides as zinc, copper or iron. In an example, ethyllignin from pine sawdust, caustic soda and ethyl chloride is given.

In the preparation of filaments of augmented strength<sup>2</sup>, the solution of cellulose ether or ester in a volatile solvent is passed through nozzles, the straight bore of which is at least 10 times the internal diameter, and thence directly through a liquid containing an organic solvent and a coagulant for the cellulose derivative, e. g. aqueous acetone, so that the threads are only slightly coagulated superficially. The threads, which may be stretched during spinning, are then solidified in the usual air-spinning space. It is alleged that in the dry-spinning of cellulose ethers and esters<sup>3</sup>, a product of especially good tensile strength is obtained by the use of nozzles of glass or quartz glass, the length of the bore of which is at least 10 times the diameter. By stretching the filaments immediately after extrusion to at least 5 times their original length, the particles (as demonstrated by Roentgen ray examination) have a better orientation therein.

In the preparation of "wood ether" (alkyl-lignins)<sup>4</sup>, when pine sawdust is etherified with (say) ethyl chloride, the ether obtained is but partially soluble in solvents (as

1. I. G. Farbenindustrie, E. P. 325512; abst. C. A. 1930, **24**, 4157; J. S. C. I. 1930, **49**, 414-B.

2. *Ibid.* E. P. 325857; abst. C. A. 1930, **24**, 4156; J. S. C. I. 1930, **49**, 504-B. F. P. 674268; abst. C. A. 1930, **24**, 2601.

3. *Ibid.* E. P. 327737; Addn. to E. P. 327671; abst. C. A. 1930, **24**, 5168; J. S. C. I. 1930, **49**, 609-B. F. P. 674269; abst. C. A. 1930, **24**, 2601.

4. *Ibid.* E. P. 330011; abst. J. S. C. I. 1930, **49**, 807-B.

benzene-alcohol, 4:1), but may be made entirely soluble by treatment with 1% aqueous chlorine dioxide for 3 days with repeated shaking. Cellulose ethers may be treated with pliability-inducing bodies and softeners such as true sulfonic acid derivatives of aliphatic or cycloaliphatic hydrocarbons containing at least 8 carbon atoms, or their salts<sup>1</sup> (ammonium sulforicinoleate, sodium sulfonate of "tall oil," palmitosulfonic acid, undecylenosulfonic acid, oleosulfonic acid, butyl oleosulfonate). The sulfonates may be added to the baths during manufacture, as in the etherification step.

Resins obtained by condensing acylated polyhydric alcohols (glycerol, sorbitol, pentaerythritol), in which at least one free hydroxyl group is retained, with polybasic carboxylic acids (phthalic, succinic, maleic, diglycollic, salicylacetic, chlorphthalic, abietic, linoleic, ricinoleic, naphthenic, lauric), and these are incorporated with cellulose ethers (ethyl-, ethylbutyl-, benzyl-cellulose) in organic solvents. Examples, ethylcellulose with the resin from phthalic acid and glyceryl mono- or di-linoleate or ricinoleate, or colophony glyceride, or *b*-hydroxyethyl linoleate; benzylcellulose with the resin from glycerol, colophony, palmitic acid, and maleic acid<sup>2</sup>.

In the manufacture of coatings<sup>3</sup>, water-insoluble cellulose ethers are mechanically finely dispersed in water and mixed with aqueous emulsions of assistants (dissolving, softening, or gelatinizing agents or mixtures of these), in amounts insufficient for homogenizing the mixture. The assistant emulsions are preferably prepared with the use of protective colloids, e. g. methylcellulose or gelatin, or of wetting or emulsifying agents, e.g. alkylnaphthalene sul-

1. I. G. Farbenindustrie, E. P. 336250; abst. Silk J. & Rayon World, 1931, **7**, #80, 54. In this connection see E. P. 26928, 1910; 288612, 303917, 306052, 326815.

2. *Ibid.* E. P. 330895; abst. J. S. C. I. 1930, **49**, 958-B. See E. P. 303915, 320041. F. P. 687119; abst. C. A. 1931, **25**, 833. See G. Schultz, Farbstofftabellen, 1923, No. 73. See F. P. 685163; abst. C. A. 1930, **24**, 163. See Belg. P. 366433.

3. *Ibid.* E. P. 330897; abst. J. S. C. I. 1930, **49**, 828-B. See E. P. 330957.



fonic acid salts or resins (sodium butylnaphthalenesulfonate). Coloring matters and rubber lattices may be added.

In the smoothing and sizing of paper<sup>1</sup>, the latter is first coated with a cellulose ether or ester which is impermeable to the smoothing agent. A lacquer for the protection of metal surfaces against corrosion comprises a solution of benzylcellulose in alcohol<sup>2</sup>, a heavy metal salt of an organic acid of high molecular weight (copper naphthenate, ferric stearate, copper oleate, lead naphthenate, ferric laurate, ferric resinate). Example, benzylcellulose 15, copper naphthenate 5 (or ferric stearate 2), triphenyl phosphate 6-9, benzene 50, xylene 50, alcohol 10.

Azo dyes may be formed in substance or on the fiber<sup>3</sup> (which may be cellulose ethers or esters) by coupling a diazo, tetrazo or diazoazo compound free from sulfonic, hydroxy or carboxyl groups with 2'.3'-hydroxynaphthoyl-4-amino-1-alkoxymethylbenzene. 60 different combinations are detailed in the patent.

On leaving the spinning nozzles<sup>4</sup>, liquid threads of cellulose ether or ester in a volatile solvent with or without a swelling agent, are treated for a short time with a volatile liquid or vapor capable of swelling the cellulose derivative without completely coagulating it, while being stretched, and are then solidified by evaporation of the volatile material. To increase their resistance to wear and exposure to weather, acids and alkalis<sup>5</sup>, mixed cotton and wool fabrics, wood and paper, are impregnated with solutions in organic solvents of water-insoluble cellulose ethers (ethyl-

1. I. G. Farbenindustrie, E. P. 327635; Addn. to E. P. 310340; abst. C. A. 1930, **24**, 5159; J. S. C. I. 1930, **49**, 656-B. E. P. 310340; abst. C. A. 1930, **24**, 726; J. S. C. I. 1930, **49**, 505.

2. *Ibid.* E. P. 323525; abst. J. S. C. I. 1930, **49**, 204-B.

3. *Ibid.* E. P. 336938; abst. C. A. 1931, **25**, 2002. See E. P. 6379, 1912; 17279, 1913; 195600, 200739.

4. *Ibid.* E. P. 327420; abst. C. A. 1930, **24**, 5158; J. S. C. I. 1930, **49**, 656-B. F. P. 677663; abst. C. A. 1930, **24**, 3369; Cellulose, 1930, **1**, 198. In this connection see E. P. 318646; F. P. 672301; abst. C. A. 1930, **24**, 2293.

5. *Ibid.* E. P. 335247; abst. C. A. 1931, **25**, 1392; J. S. C. I. 1930, **49**, 1148-B. See E. P. 322768.

cellulose) and bituminous substances (coal pitch, petroleum pitch), in such dilution that the pores remain free.

In the production of threads by the dry-spinning method<sup>1</sup>, cellulose ethers or esters containing benzene and alcohol in addition to the usual solvents, are heated before spinning to near the point at which they begin to boil within the nozzle, and are extruded into a chamber where the threads produced meet a countercurrent of air containing the vaporized solvent. Lithographic inks containing cellulose ethers are formed with resins and pigments in addition to the plasticizer for the ether, ethyleneglycol monosalicylate being specified<sup>2</sup>. In the fabrication of thermoplastic masses<sup>3</sup>, ethyl-, ethylbenzyl- and ethylbutyl-celluloses have been protected, the ethers being plasticized by such bodies as sodium butylnaphthalenesulfonate, butyl stearate, butyl phthalate and dibutyl phthalate.

Ethylcellulose alone or in conjunction with caoutchouc dissolved in specified petroleum fractions has been brought forward as a superior celluloid substitute<sup>4</sup>. Other similar ethylcellulose solvents<sup>5</sup> are mixtures of saturated or unsaturated hydrocarbons obtained by polymerization of olefines or gases containing olefines at a high temperature. In the production of polysaccharide ethers (butyl starch, ethyl starch) the ether, after formation, is esterified with a carboxylic acid above C<sub>8</sub> (benzoic, salicylic, phenylacetic, undecylic, lauric, palmitic, stearic, oleic, linoleic, abietic), mixed polysaccharide and cellulose ether-esters being produced. The specific examples given show the production of butylstarch linoleate, ethylcellulose caprate, ethylcellulose cap-

1. I. G. Farbenindustrie, E. P. 327423; abst. C. A. 1930, **24**, 5158; J. S. C. I. 1930, **49**, 655-B.

2. *Ibid.* E. P. 335074; abst. C. A. 1931, **25**, 1399; J. S. C. I. 1930, **49**, 1120-B.

3. *Ibid.* F. P. 685162. See E. P. 330957; abst. Nitrocellulose, 1931, **2**, 104.

4. *Ibid.* F. P. 682540; abst. Kunst. 1931, **21**, 45. Cf. F. P. 643413, and Addn. dated 7th Jan. 1929; 2nd Addn. dated Mar. 12, 1929; F. P. 645335; and Addn. dated Feb. 23, 1929.

5. *Ibid.* F. P. 681677; abst. C. A. 1930, **24**, 4343. F. P. 626117, and Addn. 35190. F. P. 682540.

rylate, ethylcellulose benzoate, benzylcellulose linoleate, ethylcellulose stearate and butylcellulose linoleate. They are products useful for the production of lacquers and varnishes and for the preparation of plastic masses<sup>1</sup>.

Coating compositions suitable for application to wood, natural and imitation leather and fabrics<sup>2</sup> are obtained by emulsifying solutions of water-insoluble cellulose ethers in substantially water-insoluble organic solvents (ethyleneglycol monobutyl ether, dibutylnaphthalenesulfonic acid, tri-*n*-butyl phosphate) with aqueous solutions of colloids. Example, ethylcellulose 10, benzene 35, toluene 20, xylene 20, monoethyl-ethyleneglycol acetate 10, ethyl alcohol 5, tricresyl phosphate 2.

Ethylcellulose and/or cellulose laurate are dissolved at an elevated temperature in a fatty acid, a fat and a hydrocarbon solid at ordinary temperatures<sup>3</sup>, and used for the manufacture of sealing wax and crayons<sup>4</sup>. Ethylbenzylcellulose, ethylnitrobenzylcellulose and ethylbrombenzylcellulose in which etherification has not been carried to the maximum<sup>5</sup>, are acetylated in the usual manner, forming the corresponding acetates. Monoethyl-1.5-acetylcellulose, containing about 1% benzyl, obtained by this method, is soluble in acetone, ethyl acetate and chlorinated hydrocarbons, and suitable for the manufacture of films and threads.

In comminuting ethyl-, ethylbenzyl- and ethylbutylcellulose in fibrous condition<sup>6</sup>, they are first subjected to mechanical tearing by friction (optionally in the presence of a resin or non-solvent liquid containing insufficient sol-

1. I. G. Farbenindustrie, E. P. 334897; abst. Br. Plastics, 1931, **2**, 317; J. S. C. I. 1930, **49**, 1146-B. F. P. 695323; abst. C. A. 1931, **25**, 2866.

2. *Ibid.* E. P. 334567; abst. C. A. 1931, **25**, 1108; J. S. C. I. 1930, **49**, 1079-B. See E. P. 298705, 285355.

3. *Ibid.* E. P. 325014; abst. C. A. 1930, **24**, 3868; J. S. C. I. 1930, **49**, 470-B. Can. P. 298013.

4. F. P. 683688; abst. C. A. 1930, **24**, 4631. Cf. F. P. 35939; Addn. to 615876; abst. C. A. 1930, **24**, 4155.

5. *Ibid.* E. P. 331903; abst. C. A. 1931, **25**, 204; J. S. C. I. 1930, **49**, 900-B; Br. Plastics, 1930, **2**, 230.

6. *Ibid.* E. P. 330957; abst. C. A. 1930, **24**, 6013; J. S. C. I. 1930, **49**, 814-B. Cf. Schultz, Farbstofftabellen, 1923, No. 173.

vent for gelatinizing the cellulose derivative), in the absence of solid foreign matter chemically attacking the cellulose compound. Mixed carbohydrate ethers are obtainable by heating cellulose at about 120° with methyl or ethyl chloride, and a chloride containing 3 or more carbon atoms (propyl, butyl, amyl), in the presence of an alkali hydroxide. Methylpropyl, ethylpropyl, methylbutyl, ethylbutyl, methylamyl and ethylamyl-cellulose are obtained, films produced therefrom being very little effected by water<sup>1</sup>. Whereas films from methylethylcellulose exhibit a high capacity for stretching under water, films from ethylbutylcellulose have a low water-stretching capacity.

In the manufacture of varnishes containing cellulose ethers<sup>2</sup>, resins obtained from formaldehyde and polyvinyl compounds (polyvinyl acetate, chloride, chloracetate) are combined with ethylcellulose. Wood or paper may be joined to wood, paper or metal<sup>3</sup> by sheets composed of ethylcellulose which soften at a high temperature, cellulose naphthenateoleate being also used.

Cellulose ethers and esters are dyed by treating them with arylamides of 2,3-hydroxynaphthoic acid in an alkaline bath containing organic solvents miscible with water<sup>4</sup>, which constitute solvents or swelling agents for the ethers, and which are at the same time capable of dissolving the arylamides and their alkali salts. Example, 4'methoxydiphenylamine-4-diazonium chloride. Or<sup>5</sup>, the coloring

1. I. G. Farbenindustrie, E. P. 328865; abst. C. A. 1930, **24**, 4931; J. S. C. I. 1930, **49**, 457-B. F. P. 684330; abst. C. A. 1930, **24**, 5496. (O. Leuchs and E. Doerr) D. R. P. 522171; abst. C. A. 1931, **25**, 3167. See E. P. 164374. F. P. 668686; abst. C. A. 1930, **24**, 1650.

2. F. P. 680877. In this connection see Farbw. vorm. Meister, Lucius and Bruening, D. R. P. 371147; Addn. to 364040; abst. J. S. C. I. 1923, **42**, 613-A, 1140-A. D. R. P. 403284; abst. J. S. C. I. 1925, **44**, 216-B. Chem. Fabr. Griesheim Elektron, F. P. 474086; abst. J. S. C. I. 1915, **34**, 724. I. G. Farbenindustrie, F. P. 661059.

3. *Ibid.* F. P. 679607; abst. C. A. 1930, **24**, 3868.

4. *Ibid.* F. P. 691216; abst. C. A. 1931, **25**, 1092. See Chem. Fabr. Griesheim Elektron, F. P. 476852; abst. J. S. C. I. 1916, **35**, 357. E. P. 17272, 1914; abst. J. S. C. I. 1915, **34**, 957.

5. *Ibid.* F. P. 689462; abst. C. A. 1931, **25**, 1107. See Soc. Chim. des Usines du Rhone, F. P. 619764; abst. J. S. C. I. 1928, **47**, 188.

matter may be formed in a solution of the alkylcellulose in a suitable solvent, which is subsequently removed by evaporation; e.g. a blue product is obtained by adding potassium ferrocyanide to a well stirred mixture of the cellulose compound in acetone with ferric chloride solution, while a yellow color results by using cadmium sulfate and sodium sulfide. To one familiar with qualitative inorganic analysis, many other combinations will be suggested.

A composition for the production of coatings on porous materials consists of emulsions of cellulose derivatives in aqueous solutions of organic colloids soluble in water<sup>1</sup>, capable of forming films in the presence of supplying agents. Thus, a nitrocellulose varnish is emulsified in a solution of methylcellulose in water, and dibutyl phthalate added. Other solvents specified include butylglycol ether, camphor, cyclohexanone, sodium butylnaphthalenesulfonate, tri-*n*-butyl phosphate and monoethyl ether of ethylene glycol. Vat dyes are printed and fixed next to aniline black and other colors produced on the fiber by oxidation<sup>2</sup>, by printing the vat dyes mixed with a solution of cellulose ethers or esters as a thickening agent.

Carbohydrates as cellulose, sugar, starch and dextrin are etherified by alkalis and alkylating agents (methyl or ethyl chloride or bromide)<sup>3</sup> in the presence of a desiccating agent (calcium chloride) which is kept separate from the reaction mixture. In the preparation of mixed cellulose ethers (oxyalkylcelluloses)<sup>4</sup>, as benzyloxyethyl-, benzyl-oxybutyl-, and propyloxyethyl-cellulose, a simple and substituted alkyl halide and ethylene oxide or homologue is

1. I. G. Farbenindustrie, F. P. 688315; abst. C. A. 1931, **25**, 834. See U. S. P. 1780883.

2. *Ibid.* F. P. 675045; abst. C. A. 1930, **24**, 2897. See F. P. 578690.

3. *Ibid.* F. P. 676344; abst. C. A. 1930, **24**, 2914. O. Leuchs and I. G. Farbenindustrie A. G., U. S. P. 1746663; abst. C. A. 1930, **24**, 1759; J. S. C. I. 1930, **49**, 1127-B; *Plastics*, 1930, **6**, #9, 519. Cf. E. P. 302191. D. R. P. 492319.

4. *Ibid.* F. P. 686598; abst. C. A. 1931, **25**, 592. See F. P. 687119.

brought in contact with alkalicellulose under the usual etherifying conditions.

Varnishes, mastics and paints are made from aqueous dispersions of cellulose ethers in admixture with aqueous emulsions of gelatinizing or softening agents<sup>1</sup>. Thus, a varnish is prepared by emulsifying dibutyl phthalate in water containing methylcellulose and mixing this with nitrocellulose, ocher and water. Carbohydrate ethers (ethyl-, benzyl-, benzylmethyl-cellulose) are prepared by etherifying alkalicellulose with compounds of halides in the presence of neutral salts in water. A method for the preparation of ethyl-starch is given<sup>2</sup>.

The ground layer of photographic films is made from mixed cellulose ethers and esters (cellulose acetostearate and acetophosphate, ethylcellulose stearate)<sup>3</sup>, which are mixed with acetone, water and benzene, and rolled out in the usual way.

Ethers and esters of cellulose<sup>4</sup> are dyed by the monazo dye obtained by coupling the diazo compounds of dinitroaminophenol with unsulfonated and non-carboxylated aminophenol in the presence of a salt, and developing the dye in the fiber. Example, the dye obtained by the soda alkali coupling of 4.6-dinitro-2-amino-1-hydroxybenzene and 1-amino-8-hydroxynaphthalene is dissolved in water and sodium sulfate added. The solution colors cellulose derivatives black.

A bleach-out photographic process has been patented<sup>5</sup> in which a fixable layer is prepared with the use, as the vehicle for the bleach-out dye, of a mixture of a substance

1. I. G. Farbenindustrie, F. P. 685163; abst. C. A. 1930, **24**, 6040. See F. P. 687119; abst. C. A. 1931, **25**, 833.

2. G. Balle, D. R. P. 494917; abst. C. A. 1930, **24**, 3646. See D. R. P. 492062; abst. C. A. 1930, **24**, 2599. F. P. 669256; abst. C. A. 1930, **24**, 1740. E. P. 305946; abst. C. A. 1929, **23**, 5040.

3. M. Hagedorn, D. R. P. 501643; abst. C. A. 1930, **24**, 4721. Cf. F. P. 581160, 619861.

4. W. Hentrich, D. R. P. 495620; abst. C. A. 1930, **24**, 3656.

5. B. Wendt and H. Bincer, D. R. P. 498028; abst. C. A. 1930, **24**, 4721.

which dissolves the dye, with one which does not dissolve it, but which swells in the fixing agent employed. Thus, a layer may comprise a mixture of ethylbenzylcellulose and nitrocellulose sensitized with diethylthiosinamine, the layer being fixed with a mixture of benzene and anisole (3:1). In dyeing cellulose ethers and esters<sup>1</sup>, monazo dyes are used prepared from a diazo component not containing more than one sulfo group and a monacyl-*m*-phenylenediamine.

Dyes giving yellow to red-brown shades on cellulose ether and ester fibers<sup>2</sup>, are prepared by condensing *p*-aminodiphenylamine with such bodies as methyl 4-chlor-3.5-dinitro-1-benzoate or 4-chlor-3.5-dinitro-1-benzoic acid. A brown color is produced by using a dye free from sulfonic groups<sup>3</sup>, formed by the condensation of *p*-aminodiphenylamine with dinitrohaloaryl groups. Plastic masses are formed by admixing cellulose ethers and esters in solution<sup>4</sup> with high-boilers as ethyl methylpropylacetate, ethyl methylisobutylacetate, colophony glyceryl ester (glyceryl abietate) and linseed oil.

Films, folios and coatings insoluble in water and difficult to swell<sup>5</sup>, are prepared from methyl- and ethyl-cellulose and albuminous material in the presence of ammonia. Thus, a mixture of methylcellulose solution, tannin, ammonia and water are poured on a glass plate to form a film. Similarly<sup>6</sup>, solutions containing a water-soluble cellulose ether and a tanning agent are prepared with an aqueous organic solvent. Thus, an aqueous solution of methylcellu-

1. H. Eichwede, E. Fischer and E. Mueller, D. R. P. 501443; abst. C. A. 1930, **24**, 4642.

2. H. Wagner, D. R. P. 504247; abst. C. A. 1930, **24**, 5506. See E. P. 193866, D. R. P. 493456.

3. E. Fischer and C. Mueller, D. R. P. 505885; abst. C. A. 1931, **25**, 1101; Chim. et Ind. 1931, **25**, 957.

4. O. Jordan, D. R. P. 506677; abst. Nitrocellulose, 1930, **1**, 225. See Color Index, Suppl. 1928, 54.

5. K. Daimler, K. Sponsel and G. Balle, D. R. P. 508930; abst. C. A. 1931, **25**, 1046; Kunst. 1931, **21**, 45; Chim. et Ind. 1931, **25**, 958.

6. H. Persiel, D. R. P. 509067; abst. C. A. 1931, **25**, 1083; Chim. et Ind. 1931, **25**, 1208; Kunst. 1931, **21**, 46. See E. P. 181392, F. P. 447974, 686598. D. R. P. 406081.

lose may be mixed with an alcoholic solution of tannin in aqueous propyl alcohol, and used for coatings and filaments.

Films and filaments are prepared from cellulose ethers soluble in cold water but insoluble in hot<sup>1</sup>, by extruding a cold solution into hot water as a precipitant. Violet dyeings are produced by coupling with 2,3-hydroxynaphthoic acid or its arylamino derivatives, the diazo compounds from diaryl or dialkyl ethers of 4-amino-6-acylaminoresorcinols. Coupling is effected on the cellulose ether to be dyed. Example, 4-amino-6-resorcinol dimethyl ether with<sup>2</sup> 2,3-hydroxynaphthoic acid. In the formation of cellulose ether-esters<sup>3</sup>, an alkyl cellulose containing not more than 1.5 alkyl groups is acylated in the presence of a small quantity of a catalyst so as to yield a product in which a total of 2-2.5 hydroxyl groups of the cellulose molecule (C<sub>6</sub>) are substituted. Methods for the preparation of monoethylcellulose acetate and methylcellulose acetate are given. Paper is treated on the side to be subsequently glazed<sup>4</sup> with a solution of starch to which a water-soluble dimethylcellulose has been added.

Fast blue dyeings are produced on cellulose ethers and esters<sup>5</sup> by coupling with 2,3-hydroxynaphthoic acid or its arylides the diazo compounds from dialkyl, diaryl or diaralkyl ethers of 2-amino-5-acylaminohydroquinones, coupling being effected on the material to be dyed. Mixed cellulose esters or ether-esters<sup>6</sup>, are prepared by treating a cellulose ester or a water-soluble cellulose ether containing reactive

1. K. Sponsel and G. Balle, D. R. P. 509304; abst. C. A. 1931, **25**, 1083; Kunst. 1931, **21**, 93; Chim. et Ind. 1931, **25**, 958.

2. H. Wagner, A. Kuchenbecker, R. Huss and C. Mueller, D. R. P. 509401; abst. C. A. 1931, **25**, 421.

3. E. Teupel, D. R. P. 510424; abst. C. A. 1931, **25**, 1083; Chim. et Ind. 1931, **25**, 1214; Kunst. 1931, **21**, 46.

4. K. Franz, D. R. P. 510855; abst. C. A. 1931, **25**, 1085.

5. H. Wagner, A. Kuchenbecker, R. Huss and C. Mueller, D. R. P. 511205; Addn. to D. R. P. 509401; abst. C. A. 1931, **25**, 1685; Chim. et Ind. 1931, **25**, 1218.

6. M. Hagedorn, O. Reichert and E. Guehring, D. R. P. 511208; abst. C. A. 1931, **25**, 1379; Chim. et Ind. 1931, **25**, 1214. See D. R. P. 93009, 179947, 332203, 510424. F. P. 581160. R. Wolfenstein and E. Oesser, Die Kunsteide, 1925, **1**, 2, 27, 74. Cf. Zts. ang. Chem. 1921, **34**, 646; 1924, **37**, 218.



hydroxyl groups with acid chlorides (phosphorus trichloride, benzoyl chloride, silicon tetrachloride, phosphorus oxychloride). The ester or ether is used in solution, or swollen in an organic solvent. Examples are given describing the preparation of cellulose acetophosphate, nitrobenzoate and phospholaurate (laurate-phosphate); ethylcellulose silicate and phosphate.

In order to obtain a mat effect with cellulose ethers<sup>1</sup>, the latter in solution is admixed with urea and tragacanth with or without coloring matter. G. Balle and K. Sponsel<sup>2</sup> produce plastic celluloid-like masses by working up together nitrocellulose, soluble methylcellulose and camphor. A high-boiling, non-volatile alcohol (glycol, glycerol, benzyl alcohol, cyclohexanol, borneol) may be added. In dyeing cellulose ethers and esters<sup>3</sup>, alkylated, arylated or aralkylated ethers or thioethers of the anthraquinone series, containing no additional chromophoric groups are used. Cellulose derivatives are colored golden-yellow, greenish-yellow and orange by neutral soap pastes containing respectively 1.4-dimethoxy-, 1.4.8-trimethoxy-, -anthraquinone and -anthraquinone-1.4-dithioldimethyl ether.

Cellulose ethers and esters are dyed in yellow shades by means of 4-aminonaphthalimide or its derivatives<sup>4</sup>, in which an alkyl, aryl or aralkyl group replaces H in the imino group. Thirteen examples are given. Cellulose ether plastics are formable by combining (say) ethylcellulose with terpenes (borneol, isoborneol, fenchol) in the presence of such high-boilers as benzyl alcohol and isobutyl phthalate<sup>5</sup>. Upon reacting upon alkal cellulose with an alkyl halide of the group consisting of saturated, unsaturated and

1. R. Fischer, D. R. P. 512399.

2. G. Balle and K. Sponsel, D. R. P. 512912; abst. C. A. 1931, **25**, 1350; *Chim. et Ind.* 1931, **25**, 1218.

3. I. G. Farbenindustrie, A. G., D. R. P. 514952; abst. C. A. 1931, **25**, 2303.

4. W. Eckert and C. Mueller, D. R. P. 515029; abst. C. A. 1931, **25**, 1685; *Kunst.* 1931, **21**, 94.

5. I. G. Farbenindustrie, Aust. P. 118635; abst. *Kunst.* 1931, **21**, 93.

substituted alkyl halides, mixed cellulose ethers result<sup>1</sup> soluble in chloroform, diethylenedioxide and benzene, insoluble in benzine, methyl or ethyl alcohol and ether.

Coating compositions have been described<sup>2</sup>, comprising a cellulose ether in combination with a resinous condensation product of a polybasic acid containing at least 4 carbon atoms. In a process for uniting sheets of paper, wood or cardboard<sup>3</sup>, a carbohydrate ether or ester is employed in conjunction with a cellulose ester. Films of unusual clarity are alleged to be producible<sup>4</sup> by using a cellulose ether of 2.5 ethoxyl groups dissolved in carbon bisulfide 84, ethyl ether 16. In forming colored masses suitable for lacquers, cellulose ethers or esters in the fibrous condition are first mixed with water<sup>5</sup>, a mixture of high-boiling solvent (diethyl phthalate) and coloring matter (Berlin blue) added, and the mass reduced to the dry condition. Suitable solvents are then added to produce a solution of the viscosity and total solids desired. In a similar process<sup>6</sup>, the water-wet cellulose ether or ester is kneaded with a medium which includes gelatinizers and softeners, raw or blown castor, linseed or tung oil and volatile solvents.

Fabrics such as those containing cellulose ether silk<sup>7</sup> may be printed with water-insoluble aminoanthraquinones or their derivatives other than vat dyes, and hydroxyethylamines, as the triethanolamine of commerce. An alkali-insoluble benzylcellulose is prepared by treating cellulose with 18-20% NaOH solution, pressing until the mass is 2.5-4

1. I. G. Farbenindustrie, Can. P. 304221.
2. *Ibid.* Can. P. 304969.
3. *Ibid.* Can. P. 306972.
4. *Ibid.* Swiss P. 140429; abst. Kunst. 1931, **21**, 70.
5. *Ibid.* Swiss P. 140728; Addn. to Swiss P. 113741; abst. Nitrocellulose, 1931, **2**, #5, 104.
6. Imperial Chemical Industries, Ltd., and B. Foster, E. P. 331837; abst. J. S. C. I. 1930, **49**, 872-B; Br. Plastics, 1930, **2**, #17, 100. Compare E. P. 293435, F. P. 687597; abst. C. A. 1931, **25**, 786.
7. Imperial Chemical Industries, Ltd., A. Shepherdson and L. Smith, E. P. 330652; abst. C. A. 1930, **24**, 6033; J. S. C. I. 1930, **49**, 762-B. F. P. 686428; abst. C. A. 1931, **25**, 605. Compare E. P. 211720.

times that of the original cellulose, maturing at a temperature of 22-35°, adding 50-100 parts of solid NaOH per 100 parts cellulose<sup>1</sup>, then benzylating. In order to increase the solubility in cheap solvents such as benzene, toluene or xylene mixed with "industrial spirits" (denatured ethyl alcohol)<sup>2</sup>, benzylcellulose is treated with a further amount of benzyl chloride in the presence of water or steam to improve the solubility and reduce the viscosity.

1-Hydroxy-3-amino-2,4-dimethylbenzene is condensed in the presence of sulfuric acid with a 4-mono- or di-alkylamino-2-hydroxybenzophenone-2'-carboxylic acid followed by esterification of the free carboxyl group<sup>3</sup>, or the acetaminoxyleneol may be used and the acetyl group removed during the process. Dyes are obtained suitable for coloring the cellulose ethers and esters bright bluish red. Leather, rubber or leather cloth may be finished by the application of an adhering film of an artificial resin, drying oil and cellulose ether or ester<sup>4</sup>. A process has been described<sup>5</sup> for the use of water-soluble methylcellulose (sold under the trade name of Colloresin D) for emulsion purposes.

In the production of alkylcelluloses<sup>6</sup>, the cellulose is mercerized in 18-20% NaOH solution, pressed and ripened at about 20-30° for 12-90 hours, according to the temperature used and the nature of the products desired. The alkali-cellulose formed is treated with at least 50 parts NaOH per 100 parts cellulose and then with methyl or ethyl chlorides. The ethers formed are soluble in ethylene chlorhydrin, or a mixture of alcohol and benzene or both. To produce trans-

1. Imperial Chemical Industries, Ltd., and D. Traill, E. P. 327714; abst. C. A. 1930, **24**, 5157; J. S. C. I. 1930, **49**, 610-B. F. P. 682332; abst. C. A. 1930, **24**, 4390.

2. *Ibid.* E. P. 333902; abst. C. A. 1931, **25**, 812. F. P. 690215; abst. C. A. 1931, **25**, 1081.

3. Imperial Chemical Industries, Ltd., and M. Wyler, E. P. 333016; abst. C. A. 1931, **25**, 602; J. S. C. I. 1930, **49**, 983-B. E. P. 331687.

4. *Ibid.* F. P. 686381; abst. C. A. 1931, **25**, 616. Compare F. P. 669612.

5. *Ibid.* F. P. 683728; abst. Cellulose, 1930, **1**, #10, 270. Cites E. P. 274611, 309964.

6. *Ibid.* F. P. 696158; abst. C. A. 1931, **25**, 2847.

fers with a paper base<sup>1</sup>, the latter is printed in a slowly fusible composition comprising a mixture of ethyl- or benzyl-cellulose with a resin and a plastifier (tritolyl phosphate), and is overprinted with a more readily fusible composition as rosin.

According to E. Krause and F. Wilhelmi<sup>2</sup>, paints or plastic materials of high mechanical and chemical resistance are prepared by treating fossil resins (copal, amber) with an alkali solution in the presence of organic solvents, then associating them in the dispersed phase or after precipitation and re-solution with solutions of cellulose ethers and esters. In the solubilizing of difficulty dissolvable cellulose ethers<sup>3</sup>, the ether, as ethylcellulose, is treated with depolymerizing or degrading agents (hydrochloric, sulfuric, phosphoric, oxalic acid, zinc chloride) in the presence of a swelling agent (ethyl alcohol, benzene, toluene). With solubility increase comes a corresponding viscosity decrease.

It is claimed by T. Lieser<sup>4</sup> that treatment of methylcellulose with a mixture of acetic acid and anhydride containing sulfuric acid at 25-30° for 7-20 days<sup>5</sup> gives about 50% cellobiose octa-acetate, indicating that some of the glucose anhydride units in the original product are not methylated, no methylcellobiose acetate being detected.

According to L. Lilienfeld<sup>6</sup>, rayon is produced by incorporating substances capable of providing one or more substituted or non-substituted alkyl, oxyalkyl or hydroxyalkyl radicals with a cellulose derivative containing one or more CSS- groups, the product obtained being brought

1. Kaumagraph Co., U. S. P. 1703675, 1718966. E. P. 333768; abst. C. A. 1931, **25**, 605.

2. F. P. 690987; abst. C. A. 1931, **25**, 1399.

3. O. Leuchs, U. S. P. 1767382; abst. C. A. 1930, **24**, 4307; J. S. C. I. 1930, **49**, 761-B.

4. T. Lieser, Ann. 1930, **483**, 132; abst. J. S. C. I. 1931, **50**, 74-A.

5. T. Lieser, Ann. 1929, **470**, 104; abst. J. S. C. I. 1929, **48**, 799-A.

6. E. P. 335906; abst. Silk J. 1931, **7**, #80, 52. Cites E. P. 281352, 312197, 323731, 323732.

into the appropriate shape and then dissolved by a plasticizer. 48 examples for carrying out the process are given. O-oxyalkylcellulose xanthates are obtained<sup>1</sup> (salts of dithiocarbonic-O-oxyalkylcellulose esters)<sup>2</sup>.

Cellulose ethers and their transformation products are prepared by treating cellulose first with an excess of alkali hydroxide<sup>3</sup>, then with etherifying agents. Methods for preparing ethyl- and benzylcellulose are given. Ethyl ethers of cellulose soluble in water below 16° and insoluble above<sup>4</sup>, are prepared by treating ethylcellulose soluble in water above 16° with alkali hydroxide, the mixture containing 0.1-0.25 part of caustic alkali. Cellulose derivatives soluble in alkali but insoluble in water are obtained by the action of polyalcohol halohydrins on cellulose in the presence of alkali solutions below 50%. Example, sulfite cellulose is soaked with 18% alkali at 15-20° and treated with  $\alpha$ -mono-chlorhydrin (*v*-chlorpropyleneglycol). Or the alkalized sulfite cellulose above<sup>5</sup> may be etherified with alkyl or aralkyl agents<sup>7</sup>.

In the production of cellulose ethers, cellulose containing a moderate amount of water or alkali solution is treated with solid caustic alkali so that an alkalicellulose poor in water but containing an excess of alkali is obtained. The alkalicellulose is then etherified with ethyl chloride in an autoclave.

According to H. Mark and G. v. Susich<sup>8</sup> the X-ray investigation of methycellulose has shown that the deduc-

1. L. Lilienfeld, E. P. 335993, Division of 335906; abst. Silk J. 1931, **7**, #80, 54.

2. *Ibid.* E. P. 335994, Division of 335906; abst. Silk J. 1931, **7**, #80, 52.

3. *Ibid.* D. R. P. 488780; abst. C. A. 1930, **24**, 2291.

4. *Ibid.* D. R. P. 488781; abst. C. A. 1930, **24**, 2290. Cites E. P. 14339, 1914. Aust. P. 82837. F. P. 474793. D. R. P. 155745, 485896.

5. *Ibid.* D. R. P. 493585; abst. C. A. 1930, **24**, 2881.

6. *Ibid.* D. R. P. 496978; abst. C. A. 1930, **24**, 3646. Compare G. Bumcke and R. Wolfenstein, Ber. 1899, **32**, 2501.

7. *Ibid.* D. R. P. 499129; abst. C. A. 1930, **24**, 4157.

8. Z. physikal. Chem. 1930, **B**, **9**, 157; abst. C. A. 1930, **24**, 5480; J. S. C. I. 1930, **49**, 1098-A.

tions of K. Hess and C. Trogus<sup>1</sup> of the values 21.3 and 25.6 Å. for two of the periods of identity of the elementary cell rests on a misinterpretation of the X-ray diagram, the most probable value being  $10.3 \pm 0.2$  Å. for the period of identity along the axis of the fiber.

The W. Moss and B. White lacquer<sup>2</sup> comprises benzylcellulose, ester gum, pigment and diethyl phthalate dissolved in a solvent mixture of ethyl acetate, acetone, benzene, toluene and xylene. According to A. Nathansohn<sup>3</sup> highly polymerized ethers and esters of cellulose are made by treating the esters or ethers in a solvent with phosphorus compounds containing halogens (oxychloride, trichloride, sulfochloride), phosphine chloride, phosphine phenylchloride, phosphine diethylaminochloride, phenoxylophosphoric acid, organic bases such as pyridine, quinoline or aniline preferably being added. The products are useful for artificial filament manufacture.

In the fabrication of opaque films<sup>4</sup>, two films are superposed, one of which contains finely divided metallic powder such as gold or aluminum while the other contains an ordinary filler or opaque coloring material as zinc oxide. Cellulose ethers or esters form the substance of the film. In coating cellulose ether and ester films with metal<sup>5</sup>, the material is first immersed in a reducing bath which is free of any filling, such as pyrogallol, hydroquinone, pyrocatechol or like photographic developers in water or alcohol, which do not dissolve the film, but effect a superficial swelling of it in association with the reducing agent used. After evaporation of the solvent the reducing agent remains, the ma-

1. Z. physikal. Chem. 1929, B, **5**, 161; abst. J. S. C. I. 1929, **48**, 1222-A. See also C. Trogus and K. Hess, Z. physikal. Chem. 1929, B, **4**, 321. K. Hess and C. Trogus, Ber. 1928, **61B**, 1982.

2. U. S. P. 1815444. W. Moss, B. White and C. Dreyfus, Can. P. 302649; abst. C. A. 1930, **24**, 4647. Compare E. P. 313134.

3. F. P. 683251; abst. C. A. 1930, **24**, 4631.

4. Non-Inflammable Film Co., Ltd., and D. Phillips, E. P. 331214; abst. C. A. 1931, **25**, 178; J. S. C. I. 1930, **49**, 814-B.

5. M. Ow-Eschingen, E. P. 330677; abst. C. A. 1930, **24**, 6014. Cites E. P. 311766.

terial then being treated with a solution of a reducible metal salt as silver nitrate.

In a painting process in which the second coat is applied to the first while the latter is still wet<sup>1</sup>, the paint material for the first coat is treated with a sufficient quantity of an alkaline earth oxide or hydroxide, or of the soaps of these metals with resinic or oleic acids (calcium, barium, strontium, magnesium resinate or oleate), while the vehicle for the covering coat contains cellulose ethers and esters, thickened fatty oils or caoutchouc. In the treatment of hides, as a substitute for egg-yolk<sup>2</sup>, the hides are first treated with 10% of their weight of tanning liquor and methylcellulose as a suitable emulsifier. In the treating of drying oils<sup>3</sup>, particularly thickened linseed oil and China wood oil, they are polymerized by bubbling heated air through them, dissolved, and solutions of the cellulose ethers and esters added in the formation of varnishes and enamels. The Ruth-Aldo Co.<sup>4</sup> have patented a spinning nozzle for cellulose ether and ester filament formation.

A Schmidt has described a new tanning agent<sup>5</sup> consisting of an emulsion of an animal fat in an aqueous solution of dimethylcellulose. A plastic material for the manufacture of dental apparatus has been put forward<sup>6</sup>, comprising benzylcellulose 100, triphenyl phosphate 5, tritolyl phosphate 5, crystallizable benzene 360 and alcohol (98%) 40.

When halogenated alkylamines (chlorethyldiethylamine, chlorethylamine, chlorpropionylamine, chlorethyle-

1. M. Rensch, E. P. 326649; abst. C. A. 1930, **24**, 4945; J. S. C. I. 1930, **49**, 571B; Br. Plastics, 1931, **2**, #20, 142.

2. O. Röhm, E. P. 337524; abst. J. S. C. I. 1931, **50**, 131-B.

3. G. Ruth, A. G., and E. Asser, F. P. 694074; abst. C. A. 1931, **25**, 2011.

4. Aust. P. 117706. Cites D. R. P. 428745.

5. A. Schmidt and I. G. Farbenindustrie, A. G., U. S. P. 1780983; abst. C. A. 1931, **25**, 231.

6. Soc. Anon. Des Laboratories "Odont-Email," F. P. 683418; abst. C. A. 1930, **24**, 4597.

thylaniline) react on alkal cellulose<sup>1</sup>, and the products then treated with acylating, alkylating or aralkylating agents, ethers as diethylaminoethylcellulose and diethylaminocellulose acetate are obtained. By the action on alkal cellulose of heterocyclic compounds containing one or more NC-halogen groups (cyanuric chloride, dichlorquinazoline, dichlorphthalazine, dichlormaleic acid hydrazide, tribrompyrimidine)<sup>2</sup> or the corresponding bromides (cyanuric bromide, etc.)<sup>3</sup>, cellulose derivatives are obtained which readily dye.

New cellulose derivatives may also be formed in a manner analogous to the above<sup>4</sup> by the action of cyanohydric acid halides on alkal cellulose. The original structure of the cellulose is preserved when alkal cellulose is treated with a mixture of carbon bisulfide and alkylating or aralkylating agents, then treating the products thus obtained with organic amines (as-diethylenediamine, piperazine, benzylamine) containing at least one imido group. Thus, cellulose is treated with a mixture of ethyl monochloracetate, carbon bisulfide and rinsed, then treated with an aqueous solution of piperazine<sup>5</sup>. If instead, the alkal cellulose is treated with carbon bisulfide and allyl bromide and then subjecting the product to the action of piperazine, cellulose ethers are obtained of strong affinity for dyestuffs and useful for the manufacture of artificial filaments<sup>6</sup>.

1. Soc. Anon. Pour L' Ind. Chim. a Basle, F. P. 680956; abst. C. A. 1930, **24**, 4156. Swiss P. 141556; abst. C. A. 1931, **25**, 2288. Swiss P. 142175; abst. C. A. 1931, **25**, 2288. In this connection see F. P. 686575; abst. C. A. 1931, **25**, 591. Swiss P. 144227; abst. C. A. 1931, **25**, 4124. Swiss P. 144228, Addn. to 142175; abst. C. A. 1931, **25**, 4124.

2. *Ibid.* F. P. 687301; abst. C. A. 1931, **25**, 812. Swiss P. 142175; abst. C. A. 1931, **25**, 2288.

3. *Ibid.* Swiss P. 144228, Addn. to Swiss P. 142175; abst. C. A. 1931, **25**, 4124. E. P. 341237; abst. C. A. 1931, **25**, 5030.

4. *Ibid.* F. P. 689557; abst. C. A. 1931, **25**, 1082. Swiss P. 142175; abst. C. A. 1931, **25**, 2288.

5. *Ibid.* F. P. 686575; abst. C. A. 1931, **25**, 591.

6. *Ibid.* Swiss P. 144227; Addn. to Swiss P. 141558; abst. C. A. 1931, **25**, 4124. F. P. 684183; abst. C. A. 1930, **24**, 5496.



In printing textiles or materials containing the ethers or esters of cellulose<sup>1</sup>, the coloring matter is affixed by first printing the materials with aminoanthraquinone sulfonates (as sodium 1-methylaminoanthraquinone-4-benzylaminosulfonate) and vaporizing.

Hollow threads may be made by evaporation of solutions or pseudo-solutions of cellulose ethers and esters on supports such as artificial silk<sup>2</sup>, a liberation of gas being caused on the supports by boiling a volatile component of the solution, or by the liberation of gas previously dissolved in the solution, both being accentuated by heat and removal of pressure. Artificial silk threads composed of cellulose ethers<sup>3</sup> may be reduced in denier by stretching in the dry state while heated to a temperature which renders the thread substance plastic, softeners as triphenyl phosphate being added to increase the degree of softening. Hollow fibers may also be produced<sup>4</sup> by spinning a solution of the cellulose ether into a cell through which there is rapidly circulated a gas having a temperature substantially above the boiling point of the solvent.

Masses are formable from the cellulose ethers and esters by incorporating with them hexa- or hepta-chloropropane mixed with other solvents<sup>5</sup>. In a process of forming a multicolor screen on a film of cellulose ether or ester or on celluloid<sup>6</sup>, the surface is made receptive to dyes by applying thereto a layer of cellulose acetate without dye-inhibiting additions.

1. Soc. Anon. Pour L' Ind. Chim. a Basle, F. P. 683118; abst. C. A. 1930, **24**, 4642. Cites F. P. 591708, 681566.

2. Soc. des Usines Chim. Rhone-Poulenc, F. P. 674391; abst. C. A. 1930, **24**, 2601.

3. Soc. pour La Fabrication de la Soie "Rhodiaseta," E. P. 323846; abst. C. A. 1930, **24**, 3384; J. S. C. I. 1930, **49**, 319-B. F. P. 681429; abst. C. A. 1930, **24**, 4391. R. Herzog, Kolloid Zeits., 1924, **35**, 199; Ber. 1925, **58B**, 1259. Compare E. P. 277089.

4. *Ibid.* D. R. P. 496085; abst. C. A. 1930, **24**, 3369; Cellulose, 1930, **1**, #7, 198. Cites D. R. P. 370471.

5. Spicers, Ltd., D. R. P. 514945; abst. C. A. 1931, **25**, 2289. Compare E. P. 279139, Can. P. 275323.

6. Spicers, Ltd., J. Goldsmith, T. Baker and C. Bonamico, E. P. 334265. Cf. E. P. 217557, 321222, 322432.

A. von Wacek has investigated the methylation of beech wood and the cleavage of methylbeech wood (methyl lignin), it having been shown<sup>1</sup> that methylbeechwood is decomposed by hydrolysis by the Friedrich method into an acetone-soluble and acetone-insoluble portion, and that the latter (61-63% of the methyl lignin) seemed to consist of mostly tri- with some di-methylcellulose. To characterize these ethers without doubt, the water-soluble portion which seemed to be the purest, was degraded with methyl alcohol and hydrochloric acid under pressure and found to give 2,3,6-trimethylglucose. Freshly precipitated methyl lignin attained a maximum methoxyl content of 35.28% after 4 re-methylations. As this is also the maximum methoxyl content of primary methyl lignin precipitated from a freshly prepared solution it may be considered to represent the maximum MeO content of exhaustively methylated primary beech wood lignin.

In the A. Wacker process for cellulose etherification<sup>2</sup>, the alkylation is carried out in a rotating autoclave containing spheres or like pieces which break up and mix the materials<sup>3</sup>. In the preparation of monomethylenecellulose

1. Ber. 1928, **61B**, 1604; abst. C. A. 1928, **22**, 4808.

2. A. von Wacek, Ber. 1930, **63B**, 282; abst. C. A. 1930, **24**, 2878. See Ber. 1928, **61B**, 1604; abst. C. A. 1930, **24**, 2878. In this connection see Basler Chem. Fabrik, D. R. P. 162658; abst. J. S. C. I. 1906, **25**, 392. A. Behal and E. Choay, Compt. rend. 1894, **118**, 1339; abst. Bull. Soc. Chim. 1894 (3), **11**, 698; Jahr. Chem. 1894, **47**, 2708; J. C. S. 1894, **66**, 508. W. Carothers and J. Arvin, J. A. C. S. 1929, **51**, 2560; abst. C. A. 1929, **23**, 4438. A. Fromm, Ann. 1927, **456**, 168; abst. C. A. 1927, **21**, 3050. R. Herzog, A. Hillmer, E. Paersch and E. Hellriegel, Ber. 1929, **62B**, 1600; abst. C. A. 1929, **23**, 5039. A. Hoffman, Ber. 1878, **11**, 1455; 1879, **12**, 1371; abst. J. C. S. 1878, **34**, 871; 1880, **38**, 248. B. Holmberg, Ber. 1921, **54B**, 2389; abst. C. A. 1922, **16**, 1244. B. Holmberg and M. Sjöberg, Ber. 1921, **54B**, 2406; abst. C. A. 1922, **16**, 1244. P. Klason, Arkiv. Kemi. Min. Geol. 3, Art. 5, 1; abst. C. A. 1908, **2**, 3281. P. Klason and O. Fagerlind, Arkiv. Kemi. Min. Geol. 3, Art. 6, 1; abst. C. A. 1908, **2**, 3281. F. Koenig, Cellulosechemie, 1921, **2**, 93, 105, 117; abst. C. A. 1922, **16**, 1665. A. Pictet and M. Gaulis, Helv. Chim. Acta. 1923, **6**, 627; abst. C. A. 1923, **17**, 3019. B. Rassow and P. Zickmann, J. pr. Chem. 1929, **123**, 189; abst. C. A. 1930, **24**, 721. F. Semmler, Ber. 1908, **41**, 2556; abst. C. A. 1908, **2**, 2807, 3077.

3. A. Wacker Ges. Elektrochemische Ind., F. P. 677745; abst. C. A. 1930, **24**, 3368.

F. Wood<sup>1</sup> claims the methylene group substitutes two atoms of hydrogen in the adjacent hydroxyl groups.

G. Payras<sup>2</sup> describes cellulose sulfonic ethers obtained by treating alkalicellulose with sodium benzyl-*p*-sulfonate, and discusses the aminocellulose obtained by J. Briggs and by the I. G. Farbenindustrie. It has been found<sup>3</sup> that treatment of mercerized cotton (alkalicellulose) with toluenesulfochloride, the product contains 1.9% sulfur (i.e. one toluenesulfonyl group per 9-10 six-carbon groups) and the product then possesses considerable immunity to the action of substantive dyes. When treated with ammonia or suitable amines, the ester group is replaced by a nitrogen radicle, yielding "aminocelluloses." Treatment with nitrobenzoyl chloride leads to compounds which can be reduced to aminobenzoylcellulose, and this is also susceptible to acid dyes.

The I. G. Farbenindustrie claim<sup>4</sup> that treatment of alkalicellulose with the sodium salt of 1'-chlor-1-methylbenzenesulfonic acid (4) or (2), or 1'-chlor-1,3-dimethylbenzenesulfonic acid (4) water-insoluble cellulose ethers result of the benzylcellulose sulfonate type, applicable for the preparation of filaments and films. By the partial esterification of "tall oil"<sup>5</sup> by purification under vacuum distillation (7 mm.) fractions are obtained which upon acylation, produce excellent cellulose ether and ester solvents.

In the production of insoluble azo dyes (ice colors) on cellulose ethers<sup>6</sup>, the fiber is padded at 15-50° with a weakly alkaline 2,3-hydroxynaphthoic arylamide bath to which has been added a water-miscible organic solvent or swelling agent (pyridine, ethyl alcohol, acetone) in which the aryla-

1. J. S. C. I. 1930, **49**, 1079; Chem. Age (London), 1930, **23**, 548; abst. Nitrocellulose, 1931, **2**, 102.

2. Rev. gen. mat. Plastiques, 1930, **6**, 3. See F. P. 640687, 641043. J. Briggs, Zts. ang. Chem. 1913, **26**, 255. P. Karrer, Helv. Chim. Acta. 1926, **9**, 592.

3. P. Karrer and W. Wehrli, Helv. Chim. Acta, 1926, **9**, 591.

4. Aust. P. 117056. See E. P. 164375.

5. Oel & Fett-Chemie, G. m. b. H., Aust. P. 118235.

6. I. G. Farbenind. A.-G., E. P. 348269; abst. J. S. C. I. 1931, **50**, 801-B.

mide or its alkali salt is soluble, the quantity added being enough only to swell the cellulose ether without dissolving it. The color is developed with a diazo solution. E. Kiefer<sup>1</sup> has described a conducting brush for electrical machines as dynamos, composed of finely powdered graphite bonded together with a cellulose ether solution. In the printing of materials containing cellulose ethers<sup>2</sup>, water-insoluble azo- and nitro-substituted diphenylamine dyes are used, adding thereto up to 5% of a hydroxyethylamine (triethanolamine) to the printing paste to obtain an increased depth of shade.

W. Harrison<sup>3</sup> has discovered that in the formation of artificial silks of high tensile strength in which the threads are stretched while in a swollen plastic or semi-dissolved condition, improved results are obtained if the stretching process is carried out when the filaments contain the maximum percentage of alphacellulose. As swelling agents, zinc chloride, thiocyanates, sulfuric, phosphoric, hydrochloric and nitric acids or ammoniacal copper solution, is recommended. In rendering cellulose ether films resistant to water<sup>4</sup>, the film is treated with a water-miscible liquid capable of swelling the ether, together with a water-immiscible plasticizing agent, water-proofing and softening being simultaneous. The Societe des Usines Chimiques Rhone-Poulenc<sup>5</sup> have illustrated a method of coating tubes and other objects with a cellulose ether solution.

A plastic mass has been described<sup>6</sup> composed of synthetic rubber and condensates of erythrene, isoprene, dimethylbutadiene with artificial resins and cellulose ethers,

1. U. S. P. 1774381; abst. British Plastics, 1931, **3**, #25, 37.

2. Imperial Chemical Industries, Ltd., A. Shepherdson and L. Smith, E. P. 351056; abst. J. S. C. I. 1931, **50**, 801-B. In this connection see Ital. P. 271214, 271382, 273863, 277486.

3. E. P. 344873. Holl. P. 22730. Cites E. P. 229678, 271517, 319291.

4. Wolff & Co., and R. Weingand, E. P. 324677; abst. C. A. 1930, **24**, 3900. Ital. P. 274753. See Ital. P. 271076.

5. Swiss P. 142757.

6. I. G. Farbenind. A.-G., Swiss P. 142751. Compare Ital. P. 270550, 271648, 271899. Norw. P. 47842.

which are said to show exceptionally satisfactory wearing qualities. A cellulose ether is obtained when alkalicellulose is acted upon with a mixture of carbon bisulfide, chloracetic ether and piperazine, the product being distinguished for its affinity for acid wool dyes<sup>1</sup>. When cellulose is treated with phthalic anhydride in the presence of tertiary bases as pyridine as diluents, new derivatives result having a strong affinity for basic dyes. Example, cellulose 15 is treated for 4 hours at 60° in a mixture of pyridine 100 and phthalic anhydride, washed and dried. When phenylisocyanate is allowed to act upon cellulose<sup>2</sup>, the cellulose is outwardly unchanged, but a product results having increased affinity for basic dyes without mordants.

In the production of cellulose ether filaments<sup>3</sup>, it has been found that the tensile strength in the wet state can be considerably augmented by adding to the precipitating bath salts and colloidal substances which cause swelling as molasses, tannins, soluble starch, albuminous materials, especially suitable being sulfite waste liquor and solutions of degraded albuminous materials as degraded keratin. E. Hausheer<sup>4</sup> produces bodies of the order of cellulose dithiomethane-phenylamine (aniline) and cellulose thiomethanamine, by an illustrative example as follows: linters 100 is immersed in 18% NaOH 1000, at 15-20° for 2-24 hours, pressed to 350 parts, milled, ripened and treated for 6-48 hours with dithiomethane (carbonbisulfide). The fresh cellulose xanthate is dissolved in dilute alkali solution, filtered, and aniline 60-120 added. After several hours standing monochloracetic acid 60-120 is also added, and after 6-72 hours the cellulose thiomethanephylamine precipitates on stirring to a flocculent mass, dissolving in dilute alkali solutions and in several aliphatic and aromatic bases.

1. Soc. Chem. ind. in Basle, Swiss P. 141558.
2. *Ibid.* Swiss P. 142749. Ital. P. 274021.
3. Aceta G. m. b. H., Swiss P. 142406.
4. Swiss P. 139512.

**Etherified Cellulose Advancement Published During 1931.** Notwithstanding the financial instability, business depression and general feeling of unrest in many parts of the world evidenced often by research curtailment with a corresponding diminution in inventive ingenuity as indicated by a decrease in scientific contributions, processes perfected and products patented, the year 1931 stands out from the preceeding years in the wealth of academic papers and inventions granted in this field, as shown herein by the more than three hundred papers presented and patents issued during this twelve month period.

F. Ackermann<sup>1</sup> has described anthraquinone derivatives and processes for their manufacture, of especial affinity for colloids of the cellulose ether type, obtained from the reaction products of aromatic amines (aniline or *p*-anisidine) heated at 150-180° with such compounds as 1.5 (or 1.8-)diamino-4.8 (or 4.5)-dinitroanthraquinone and subjected to careful reduction, as with sodium sulfide or hydrosulfide. They dye cellulose ethers or esters blue to blue-green shades. It has been found that the electric charge of fibers of cellulose ethers and esters, which is formed during their transformation into textiles<sup>2</sup>, may be reduced by treating the fibers with mixtures of oils or fats to which an oil-soluble organic base has been added.

According to T. Araki and T. Nagamote<sup>3</sup> solutions of ethylcellulose in benzene and toluene are turbid, but the addition of 3.5-37.5% of alcohols renders them clear. For airplane dope, petroleum may be added as a diluent and tricresyl or triphenyl phosphates as plasticizers, but not castor oil. A proper dope consists of ethylcellulose 12, benzyl alcohol 2, benzene 60, methyl alcohol 13, no change occurring in storing such a dope for 1.5 years. As a varnish

1. F. Ackermann and C. Apotheker, U. S. P. 1792348; abst. C. A. 1931, **25**, 2005.

2. Aceta Ges., E. P. 346912; abst. Silk J. 1931, **8**, #88, 56.

3. J. S. C. I. Japan, 1930, **33**, 382-B; abst. British Plastics, 1931, **3**, #28, 63.

containing synthetic resins<sup>1</sup>, benzylcellulose is incorporated with the resin, preferably in solution, and in quantity about 5-10% of the total solids. The products formed are adapted for the manufacture of laminated and molded articles. In a comprehensive investigation upon the preparation and analysis of the benzylcelluloses<sup>2</sup>, details of the preparation and properties of *o*-chlorbenzylcellulose have been recorded, and established that in the reaction between alkalicellulose and *o*-chlorbenzyl chloride, the extent to which ether formation occurs is influenced to a marked degree by the temperature of the reaction and the alkali concentration used to prepare the alkalicellulose. With increase in either or both of these factors, an increased ether formation occurs.

Mixed ether-esters (ethylcellulose formate, diethylcellulose formate, methylcellulose formate, ethylbenzylcellulose formate) are obtainable when an alkyl ether of cellulose containing free hydroxyl groups is stirred with an excess of formic acid. The product is precipitated by pouring into a large bulk of water<sup>3</sup>. The diethylcellulose formate contains 2 mols. of ethoxyl and 0.3 mol. of formic acid in combination, being stable, waterproof and soluble in methylene chloride. In the manufacture of threads, ribbons and films<sup>4</sup> in the usual manner, they may be cleaned by simple immersion in luke warm water, if the filaments are extruded into a precipitating bath containing sodium, potassium or ammonium oleate, glycol, glycerol or cyclohexanol, hydrocarbons (decane, tridecane, hexadecane, tetralin, dekalin, terpenes, sesquiterpenes, polyprenes) or fatty alkyl esters of high molecular weight (methyl or ethyl oleate or stearate).

1. Bakelite Corp., E. P. 342286; abst. C. A. 1931, **25**, 4421. Cites E. P. 293453; abst. C. A. 1929, **23**, 1763. E. P. 324025; abst. C. A. 1930, **24**, 3387.

2. R. Ball, Thesis, McGill University, May, 1931.

3. G. Balle, H. Lange, K. Ost and I. G. Farbenindustrie, Akt. Ges., U. S. P. 1823847. E. P. 347651; abst. Silk J. 1931, **8**, #89, 54.

4. H. Barthelemy, U. S. P. 1826718. Can. P. 315966.

The elasticity of plastic materials having a basis of ethylcellulose<sup>1</sup> is increased by producing a layer free from, or poor in, plastifying agents. Thus, the article may be dipped in ether or sprinkled with a solution of ethylcellulose in benzene. As new sulfur dyestuffs for the coloring of the cellulose ethers golden yellow shades<sup>2</sup>, sodium anthraquinonyl-*b*-mercapto propionate, 5-chlor-1-anthraquinonyl-*b*-mercapto propionate and 4-amino-1-anthraquinonyl-*b*-mercapto propionic acid are examples. In the series of three patents granted to J. Bongrand and L. Lejeune<sup>3</sup> are described the manufacture of rubberized threads of textile material, the threads being first impregnated *in vacuo* or under pressure with an aqueous dispersion of rubber, followed by an aqueous dispersion of a cellulose ether, or in solution in an organic solvent. The threads show high strength, even when made from relatively short fibers. A finish suited for simultaneously sizing and dyeing cotton and artificial silk<sup>4</sup> comprises a solution of a methylated cellulose to which softening agents have been added. D. Bradner has found that the addition of potassium chloride to an ethylation mixture<sup>5</sup> containing cellulose, caustic soda and ethyl chloride is much more effective than sodium chloride (see p. 98) advocated by E. Teupel. His results show a yield from 100 of cellulose, of 116 when no chloride was introduced, 126 by the use of sodium chloride, and 134 with potassium chloride.

D. Brauns and H. Frush<sup>6</sup> have described compounds obtained by the action of HF on fructose, and detailed the constants of fructose tetracetylfluoride, 2-fluortriacetylfruc-

1. C. Boehringer & Soehne, G. m. b. H., F. P. 698321; abst. C. A. 1931, **25**, 3137.

2. H. Berthold, U. S. P. 1760806; abst. C. A. 1930, **24**, 3654.

3. E. P. 344414, 344415; abst. J. S. C. I. 1931, **50**, 535-B. F. P. 700850, 700851, 700852; abst. C. A. 1931, **25**, 3848.

4. H. Boehme, Akt. Ges., E. P. 350409; abst. Textile Mfr. 1931, **57**, 420.

5. U. S. P. 1813726; abst. C. A. 1931, **25**, 5287. Can. P. 311489. Cites E. Teupel, D. R. P. 408342.

6. Bur. Standards J. Research 1931, **6**, 449; abst. C. A. 1931, **25**, 4231.



tose, 1-methyl-2-fluortriacetylfructose and 2-fluoro-3-methyl-triacetylfructose. Before etherification, cellulosic material as linters, is pretreated with a halogen-substituted organic compound such as an acetic acid solution of phosgene, a solution of acetyl chloride in trichlorethylene, a solution of chlormethyl ether in benzene or a mixture of acetyl chloride and propionyl chloride in tetrahydronaphthalene for the purpose of increasing its reactivity<sup>1</sup>. Natural silk which is to be woven with cellulose ether or ester silk<sup>2</sup> is degummed in the yarn and then sized with agents removable by hot water (potassium, sodium, ammonium, calcium, magnesium or zinc oleates, stearates, or naphthenates).

Mixed resinous products are obtained by the condensation of furfural with benzene-, toluene-, xylene-, xylenemonomethyl-, *m*-toluenethyl-sulfonamide, forming a product soluble in the solvents of, and miscible with the cellulose ethers of value in the production of moldable combinations<sup>3</sup>. In the preparation of lacquers and adhesives<sup>4</sup>, cellulose ethers are combined with glycol esters and an arylsulfonamide-aldehyde resin. In the wet-spinning of solutions of formyl-, acetyl-, propionyl-, butyryl-, ethyl- and benzyl-cellulose<sup>5</sup>, the spinning solution is maintained at a temperature above that of the spinning bath, so that more concentrated solutions may be spun and hence smaller jet apertures used. Coagulation is effected in a suitable solvent containing a hydrocarbon or castor oil. In a variant of this method<sup>6</sup>, the coagulating bath contains at least one constituent which is insoluble or incompletely soluble in the bath (as ethylene- or methylene-dichloride), and the

1. British Acetate Silk Corp., Ltd., F. Stoyale, G. Edwards and A. Lipscomb, E. P. 340555; abst. C. A. 1931, **25**, 5030; J. S. C. I. 1931, **50**, 343-B; Silk J. 1931, **7**, #83, 52.

2. British Celanese, Ltd., E. P. 339896; abst. J. S. C. I. 1931, **50**, 341-B.

3. *Ibid.* E. P. 340102; abst. Brit. Plastics, 1931, **3**, #26, 86. Cites E. P. 315807, 315808, 340101.

4. *Ibid.* E. P. 342144; abst. C. A. 1931, **25**, 4421.

5. *Ibid.* E. P. 341148; abst. C. A. 1931, **25**, 5029.

6. *Ibid.* E. P. 341388; abst. C. A. 1931, **25**, 5028; Silk J. 1931, **7**, #84, 53.

bath maintained at a temperature above the boiling point of this component.

In the manufacture of laminated glass<sup>1</sup>, the cellulose ether used to unite the sheets is first subjected to a bleaching action as by exposure to ultra-violet rays, and may be purified by careful filtration so as to eliminate "star dust" (microscopic specks). In the filling and coating of rough and porous surfaces such as wood, ceramic materials or metals<sup>2</sup>, a filler is first applied containing a non-drying oil or fatty acid, and then coated with a cellulose ether or ester lacquer to which synthetic resins are added, both, of course, being in solution. A diphenylolcycloparaffin (as diphenylolcyclohexane) with benzylcellulose and suitable plasticizers and volatile solvents<sup>3</sup>, constitutes the lacquer preparation of the British Celanese, Ltd. Synthetic resins (condensates of phenol-aldehyde, diphenylolpropane-formaldehyde, diphenylolpropane-acetone) in conjunction with the cellulose ethers<sup>4</sup> have been brought forward as suitable glass sheet laminants on account of their property of remaining transparent and colorless upon long exposure to light. Combining cellulose ethers with the condensate diphenylolpropane-acetone produces an excellent adhesive for glass, stone or asbestos<sup>5</sup>.

Knitted cellulose ether or ester garments may be delustered by the usual methods (boiling in a soap solution or precipitating barium sulfate or zinc sulfide within the fibers) while stretched on suitable supports to avoid the formation of wrinkles and distortion<sup>6</sup>. In producing pebble or cockle effects in fabrics, they are so constructed that

1. British Celanese, Ltd., E. P. 341890; abst. C. A. 1931, **25**, 4997. Cf. E. P. 296675, 299066.

2. *Ibid.* E. P. 342211; abst. C. A. 1931, **25**, 4422.

3. *Ibid.* E. P. 342429; abst. C. A. 1931, **25**, 4421; Brit. Plastics, 1931, **3**, #25, 40.

4. *Ibid.* E. P. 342458; abst. C. A. 1931, **25**, 4374. Can. P. 315772.

5. *Ibid.* E. P. 342674; abst. J. S. C. I. 1931, **50**, 452-B; Brit. Plastics, 1931, **3**, #28, 179.

6. *Ibid.* E. P. 343698; abst. J. S. C. I. 1931, **50**, 486-B; Silk J. 1931, **8**, #85, 54.

either the warp or weft contain yarns of cellulose ethers and of non-organic cellulose derivatives. A reagent is then applied which does not appreciably effect the cellulose ether (as alkali solutions) but causes the shrinkage of the other yarn<sup>1</sup>. If it is desired to produce pile fabrics<sup>2</sup>, natural silk still containing gum is woven with cellulose ether filaments, and then submitted to a boiling-off process to remove the silk gum and otherwise not effect the luster of the natural silk, while the ether yarn is delustered, thus producing novel effects.

Lacquers are produced by combining an etherified cellulose with a resinous product obtained by the condensation of diphenylolcycloparaffin with formaldehyde in the presence of urea or toluenesulfonamide<sup>3</sup>. Best results in delustering cellulose ester or ether filaments is said to result when the thread in the hank form is entirely submerged in the delustering liquor<sup>4</sup>. It has been found that an increased amount of a polymerized vinyl compound (as vinyl acetate, vinyl propionate, vinyl butyrate) can be tolerated in a cellulose ether composition<sup>5</sup>, if a natural or synthetic resin which is compatible with the cellulose derivatives is also incorporated, the finished products being suitable as lacquers, adhesives and for photographic films.

As a coating composition for the treatment of surfaces<sup>6</sup>, an ether of cellulose is deposited on a wood, textile, metal or glass surface by evaporation of a solution of a high-boiling solvent with some water, clouded, milky or translucent coatings being formed. It is claimed that the tendency of cellulose ether and ester fabrics to slip, ladder and run may be obviated by coating them with rubber latex

1. British Celanese, Ltd., E. P. 344155; Addn. to 342075; abst. J. S. C. I. 1931, **50**, 486-B. Cites E. P. 342075.

2. *Ibid.* E. P. 344410.

3. *Ibid.* E. P. 344413; abst. C. A. 1931, **25**, 4725.

4. *Ibid.* E. P. 345509, Addn. to 343698; abst. C. A. 1931, **25**, 5580; J. S. C. I. 1931, **50**, 584-B.

5. *Ibid.* E. P. 345521; abst. J. S. C. I. 1931, **50**, 597-B; Brit. Plastics, 1931, **3**, #28, 63. See also E. P. 308658, 311657.

6. *Ibid.* E. P. 346269; abst. J. S. C. I. 1931, **50**, 685-B.

solution, preferably in the emulsion form wherein the particles are less than a micron in diameter<sup>1</sup>. Tough and pliable yarns, capable of receiving a higher twist and of being knitted more compactly<sup>2</sup>, may be prepared by extruding a solution of cellulose ether or ester in a volatile solvent, which solution also contains a non-solvent or precipitant for the cellulose derivative. The process is carried out by the dry or wet spinning methods. Colorations or colored pattern effects may be induced on cellulose ether yarns<sup>3</sup>, by applying to or removing from the materials, color in a volatilized form. Thus volatile colors may be applied intermittently or through a stencil in a current of steam or other hot vapor or gas, or locally by a transfer sheet subjected to heat and pressure, with or without a simultaneous embossing operation.

In the wet coagulation process for the manufacture of cellulose ether filaments<sup>4</sup>, there is employed a setting bath containing a relatively high proportion of solvent for the cellulose ether. The filaments upon emergence from the bath are highly plastic due to but partial coagulation. The coagulation bath may contain liquid non-solvents which are plasticizers, as triaryl phosphates, alkyl phthalates or aryl sulfonamides<sup>5</sup>. These non-solvents or high boiling solvents may also be incorporated in the spinning solution before extrusion into filament form<sup>6</sup>. In another modification<sup>7</sup>, the coagulated filaments are allowed to emerge from the spinneret orifices in a plastic state but in a partially coagulated condition, and then completing the coagulation in the usual manner by immersion in a precipitating solution. Desirable effects are said to be obtained by spinning direct

1. British Celanese, Ltd., E. P. 346511; abst. Silk J. 1931, **8**, #88, 54.

2. *Ibid.* E. P. 348625; abst. Silk J. 1931, **8**, #89, 56.

3. *Ibid.* E. P. 349683; abst. Textile Mfr. 1931, **57**, 419.

4. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 340324; abst. Silk J. 1931, **7**, #83, 52. Cf. E. P. 311790.

5. *Ibid.* E. P. 340325; abst. Silk J. 1931, **7**, #83, 52.

6. *Ibid.* E. P. 340436, Addn. to 340324; abst. C. A. 1931, **23**, 4707; Silk J. 1931, **7**, #83, 52.

7. *Ibid.* E. P. 340437, Addn. to 340324, 340325; abst. C. A.

into a coagulating bath in which is present a salt, sugar or other polyhydric alcohol, adapted to reduce the solubility of the solvent in the non-solvent coagulating medium<sup>1</sup>.

Crepe effects, particularly those containing cellulose ether or ester yarns, are produced by weaving in warp or weft, tightly twisted yarns previously impregnated with an emulsion of a swelling or gelatinizing agent and dried, and then exposing to conditions (as scouring or steaming) which promote the swelling action<sup>2</sup>. Brocade effects result from printing fabrics with swelling agents and facilitating their action similarly. British Celanese, Ltd., have described and illustrated a method for cellulose ether filament formation by the dry or evaporative method<sup>3</sup>, in which relatively small centrifugal boxes (3-4 inches diam.) are used, with relatively high revolutions (12,000-20,000 r. p. m.). In the formation of very fine deniers (0.5-1) from cellulose ether solutions<sup>4</sup>, the spinning solution is extruded into an evaporative atmosphere followed by passing the filaments after formation of an outer skin on them, into an atmosphere of solvent, and then stretching the softened filaments. An apparatus has been described for this purpose<sup>5</sup>. As a sizing for textile materials<sup>6</sup>, aqueous solutions of hydroxy- or carboxy-alkyl cellulose ethers have been advocated. Or<sup>7</sup>, the threads may be sized with a polymerized or partly polymerized vinyl compound (vinyl acetate or chloracetate).

Crepe effects are obtained on cellulose ether yarns by impregnating with a swelling agent which becomes effective

1. British Celanese, Ltd., E. P. 343062; abst. C. A. 1931, **25**, 5557.

2. British Celanese, Ltd., W. Dickie and R. Moncrieff, E. P. 356233; abst. J. S. C. I. 1931, **50**, 1008-B.

3. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 340471. F. P. 697725. Cites E. P. 340504, 340505. Abst. C. A. 1931, **25**, 3168.

4. *Ibid.* E. P. 340929; abst. C. A. 1931, **25**, 5028.

5. *Ibid.* E. P. 340930; abst. C. A. 1931, **25**, 5028.

6. British Celanese, Ltd., H. Dreyfus, W. Dickie and P. Sowter, E. P. 344528; abst. J. S. C. I. 1931, **50**, 585-B; Silk J. 1931, **8**, #86, 54.

7. British Celanese, Ltd., H. Dreyfus and W. Taylor, E. P. 346267; abst. Textile Mfr. 1931, **57**, 305.

on dilution with water, fabrics woven with tightly twisted yarns, or yarns which are afterwards woven into fabrics, and then scouring. Suitable swelling agents are salts (zinc chloride, calcium thiocyanate) or organic swelling agents (acetone, acetic acid, ethyl alcohol suitably diluted with benzene)<sup>1</sup>. The threads should be highly twisted<sup>2</sup>. To prevent creasing in liquid treatments of textile materials<sup>3</sup>, as cellulose ethers made by dry-spinning methods, the material is first thoroughly wetted out in open width form.

Cellulose ether or ester silk is dyed with the free leuco-compounds of vat or sulfide dyes or of aminoanthraquinones in aqueous suspension, preferably from a bath having pH 4-8, and the color developed by oxidation with air, black liquid, soap and sodium perborate, and especially with soap and sodium peroxide. Example, Ciba blue G, Caledon jade green, 1-benzamido-4-hydroxyanthraquinone, indophenol from *p*-aminodimethylaniline and *α*-naphthol<sup>4</sup>. The fastness of aminoanthraquinone dyeings to the combined action of light and acids is improved by treating the material with uncolored alkylated aminodiaryls (tetramethyl-4.4'-diaminodiphenylmethane, tetramethylbenzidine) or with alkylated, aralkylated or arylated carbamides, thiocarbamides or<sup>5</sup> guanidines (*s*-diisooamylthiocarbamide, tetramethylthiocarbamide) which are retained in the material during any subsequent treatment<sup>6</sup>. In the production of pattern effects on materials made of or containing cellulose ether or ester yarns<sup>7</sup>, the discharge (in printing) of dyed cellulose derivatives thread is effected by means of metallic

1. British Celanese, Ltd., and W. Dickie, E. P. 351999; abst. J. S. C. I. 1931, **50**, 880-B. See also E. P. 348589.

2. *Ibid.* E. P. 352000; abst. J. S. C. I. 1931, **50**, 880-B.

3. British Celanese, Ltd., and G. Ellis, E. P. 338190; abst. C. A. 1931, **25**, 2305.

4. British Celanese, Ltd., G. Ellis, H. Olpin and R. Storey, E. P. 341408; abst. C. A. 1931, **25**, 5042; J. S. C. I. 1931, **50**, 437-B. Compare E. P. 262506.

5. British Celanese, Ltd., G. Ellis, T. Ockman and H. Olpin, E. P. 340541; abst. J. S. C. I. 1931, **50**, 346-B.

6. *Ibid.* E. P. 340572.

7. British Celanese, Ltd., G. Ellis and W. Miller, E. P. 342333; abst. C. A. 1931, **25**, 5043; J. S. C. I. 1931, **50**, 391-B.

salts (stannous or titanous chlorides) and facilitated by the presence of potassium thiocyanate, so that complete discharge of very deep shades as navy-blue, black and brown may be obtained. To improve the penetration of reagents used in the dyeing or printing of cellulose ether and ester materials<sup>1</sup>, a benzene dihydroxy-compound (quinol, toluquinol) and their mono-ethers and halogen derivatives, are added to printing pastes, especially in discharge printing. Pyrazolone dyes, preferably unsulfonated, are stable to reducing discharges and are added to the discharge paste for colored printing of cellulose ethers<sup>2</sup>. Example, aniline, *o*-, or *p*-anisidine, or aminoacetanilide with 1-phenyl-3-methyl-5-pyrazolone. Where the coloring is done by vatting methods, the vats are maintained at temperatures below the normal atmosphere, e.g., at 0.-10°, the process being particularly suitable for dyeing acetyl- or ethyl-cellulose<sup>3</sup>. For the coloring of cellulose ethers or esters<sup>4</sup>, 1-phenyl-3-methyl-5-pyrazolone is coupled with a diazotized arylamine containing a *p*-amido or *p*-hydroxy group, to give dyes especially suitable for discharge effects with stannous chloride, examples being, *p*-aminophenol (golden-yellow), *p*-phenylenediamine (orange), *p*-aminodimethylaniline (red), *p*-aminoacetanilide (golden-orange), 4-dimethylamino-*m*-anisidine (red).

Colored discharges on cellulose ether materials dyed with azo dyes are obtained by using a discharge paste containing stannous chloride or thiocyanate, an anthraquinone dye and a swelling agent (phenol, quinol)<sup>5</sup>. Anthraquinone dyes sensitive to hyposulfites are usually insensitive to stannous salts. Resins suitable for combination with

1. British Celanese, Ltd., and G. Ellis, E. P. 346694; abst. J. S. C. I. 1931, **50**, 716-B; Textile Mfr. 1931, **57**, 306.

2. *Ibid.* E. P. 346751; abst. J. S. C. I. 1931, **50**, 716-B; Silk J. 1931, **8**, #88, 54.

3. *Ibid.* E. P. 347682; abst. Silk J. 1931, **8**, 89, 54.

4. *Ibid.* E. P. 350577; abst. J. S. C. I. 1931, **50**, 966-B.

5. *Ibid.* E. P. 351457; abst. J. S. C. I. 1931, **50**, 838-B. Cites E. P. 316989.

methyl-, ethyl- and benzyl-cellulose<sup>1</sup>, for use in films, filaments and coating compositions are made by condensing toluenesulfonamide with formaldehyde or other aldehyde, usually with a small proportion of urea, in the presence of heat in the absence of water. Materials composed of cellulose ethers are colored by immersion in a colloidal solution of a suitable metal oxide (the oxide or hydroxide of zinc, titanium, chromium, aluminum, iron, tin), whereby absorption occurs, followed by dyeing with a mordant dye<sup>2</sup>. Alternately, the order of these treatments may be reversed.

Dull-luster cellulose ether silk may be produced by spinning the usual acetone solution to which has been added 0.5-4% of finely ground titanium oxide (average particle size 0.0001-0.00035 mm.) The opacity of the resulting silk is increased by adding 2-6% (calculated on the weight of titanium oxide) of boric acid or barium borate to the titanium oxide<sup>3</sup>. Filaments obtained by coagulation of cellulose ethers in aqueous media are improved both as regards tensile strength and transparency by impregnating them with high-boiling solvents, swelling agents or plasticizers (diacetone alcohol, diethyl tartrate) and subsequently passing them round heated rollers while under tension<sup>4</sup>. Compositions useful as varnish ingredients are prepared by heating ethyl- or benzyl-cellulose with resins or/and oils to 280-300°. Thus, ester gum 1, linseed oil 2, ethylcellulose 1 may be heated at 280° until the cellulose ether has completely dissolved in the resin-oil mixture. The compositions may be dispersed in benzine, or linseed-oil varnish<sup>5</sup>.

1. British Celanese, Ltd., W. Moss and B. White, E. P. 317456.

2. British Celanese, Ltd., and R. Parkinson, E. P. 343124; abst. C. A. 1931, **25**, 4413; J. S. C. I. 1931, **50**, 485-B; Rayon Record, 1931, July 3, 421.

3. British Celanese, Ltd., R. Riley, R. Parkinson and H. Sims, E. P. 341897; abst. C. A. 1931, **25**, 5028; J. S. C. I. 1931, **50**, 391-B; Silk J. 1931, **7**, #64, 54.

4. British Celanese, Ltd., R. Roberts and L. Gregory, E. P. 338936; abst. C. A. 1931, **25**, 2567; J. S. C. I. 1931, **50**, 153-B.

5. British Celanese, Ltd., W. Whitehead and C. Dreyfus, E. P. 318630. K. Burgemeister, D. R. P. 523300; abst. C. A. 1931, **25**, 3502.



Mixed material containing a cellulose ether or ester and a vegetable fiber as cotton<sup>1</sup> is dyed black by first treating it with an aqueous suspension of *p*-aminodiphenylamine or 2,4-diaminodiphenylamine which is absorbed by the cellulose ether but not the cotton, then padding with an aniline black liquor containing aniline, hydrochloric acid, potassium chlorate and copper sulfate, drying, ageing at 40-50° for development of a black on both kinds of fibers, and finally after-chroming at room temperature for 1 hr. with aqueous sodium bichromate, sp. gr. 1.005-1.015. A process for the manufacture of emulsions of the type in which water is in the disperse phase, consists in dissolving cellulose ethers or esters in a solvent substantially insoluble in water<sup>2</sup>, and whose rate of evaporation is slower than that of water, agitating the solution with an emulsifying agent (calcium oleate), and adding to the mixture while still under agitation either water alone or containing sodium oleate. In preparing aqueous emulsions of nitrocellulose in which the solvents used are methylcyclohexanone, hexalin acetate or butyl propionate<sup>3</sup>, suitable emulsifying agents are water-soluble methylcellulose, saponin, nitrated castor oil, alginates, or isopropyl naphthalene sulfonate.

Ten patents were granted in 1931 to S. Carroll for the use of new solvents for the cellulose ethers and esters, including acetoxime<sup>4</sup>, isopropyl bromide<sup>5</sup>, iodobenzene<sup>6</sup>, acetylphenyl glycine<sup>7</sup>, *p*-brombenzaldehyde or methyl-*m*-brombenzoate<sup>7</sup>, chlorcyclohexane<sup>9</sup>, ethyl chlorcarbonate<sup>10</sup>, ethyl  $\alpha$ -brompropionate<sup>11</sup>, methyl anisate<sup>12</sup>, or tripropionin<sup>13</sup>. Mixed esters as cellulose aceto-stearate, aceto-malate, or nitro-acetate (acetonitrate) are also said to be dissolvable

1. British Celanese, Ltd., A. Mellor and D. McLellan, E. P. 351577; abst. J. S. C. I. 1931, **50**, 838-B.

2. Canadian Industries, Ltd., G. Davies and W. Jenkins, Can. P. 314396. (See p. 223, n. 7)

3. *Ibid.* Can. P. 314397. (See p. 223, n. 6)

4. S. Carroll, U. S. P. 1813660. 5. *Ibid.* U. S. P. 1813661.

6. *Ibid.* U. S. P. 1813662. 7. *Ibid.* U. S. P. 1826687.

8. *Ibid.* U. S. P. 1826688. 9. *Ibid.* U. S. P. 1826689.

10. *Ibid.* U. S. P. 1826690. 11. *Ibid.* U. S. P. 1826691.

12. *Ibid.* U. S. P. 1826692. 13. *Ibid.* U. S. P. 1826693.

by the above. In the dry-spinning of cellulose ether and ester filaments<sup>1</sup>, a temporary increase in pressure at the jets to assist in starting the spinning is obtained by cutting off the solution from the jets and supplying it to a pressure chamber into which it is pumped until the desired pressure has been obtained, whereupon the pressure chamber is put into communication with the jets. In addition to their patent on lacquer coated cellophane, W. Charch and K. Prindle have more recently taken out a patent<sup>2</sup> on the coating composition per se, and a patent<sup>3</sup> on the method of drying the coating and rendering the resultant wrapping material flexible. W. Charch and N. Craigie have also taken out related patents, one<sup>4</sup> covering an apparatus for coating a sheet of regenerated cellulose having beaded edges and the other<sup>5</sup> for a method of applying a wax containing coating thereto.

For the direct production of colored cellulose ether fibers<sup>6</sup>, the spinning solution comprises a dissolved cellulose derivative which has already been dyed, as by close contact with a mineral powder intimately subdivided and in the presence of a liquid capable of being absorbed by the cellulose ether to an extent insufficient to produce any observable change in the latter. Water-insoluble cellulose ethers may be colored by stirring the powdered ether and powdered preformed pigment together in a liquid cellulose solvent with an equal volume of water<sup>7</sup>. Films and threads having a mat surface are made from a mixture of acetylcellulose in acetone and benzylcellulose (or ethylcellulose) in a mixture of acetone, benzene, and methyl or ethyl alcohol<sup>8</sup>.

1. Cellulose Acetate Silk Co., Ltd., and H. Curtis, E. P. 344591; abst. Silk J. 1931, **8**, #86, 54.

2. W. Charch and K. Prindle, U. S. P. 1826696.

3. *Ibid.* U. S. P. 1826699; abst. C. A. 1932, **26**, 537.

4. U. S. P. 1826697.

5. U. S. P. 1826698.

6. L. Clement and C. Riviere, E. P. 350894; abst. Textile Mfr. 1931, **57**, 422.

7. *Ibid.* E. P. 350924; abst. J. S. C. I. 1931, **50**, 877-B; Textile Mfr. 1931, **57**, 422. F. P. 704499; abst. C. A. 1931, **25**, 4705.

8. *Ibid.* F. P. 700477; abst. C. A. 1931, **25**, 3834.

In spinning downward by the dry-spinning process<sup>1</sup>, the whole of the evaporative atmosphere is introduced into the spinning cell in the neighborhood and on one side of the extrusion nozzle, and is then withdrawn from the cell on the opposite side of the nozzle at or below its level, the whole of the evaporative atmosphere being thus drawn across the extrusive nozzle, this method being designed for the preparation of cellulose ether or ester filaments.

In the manufacture of cellulose ether nitrates (dimethylcellulose nitrate, diethylcellulose nitrate) the cellulose ether is dissolved in diacetyl-*o*-nitric acid, forming a clear viscous solution. On addition of a dehydrating agent as acetic anhydride, the cellulose ether is nitrated in a few minutes. These ethers dissolve in a large number of solvents<sup>2</sup>. A review of processes for cellulose ether and ester artificial filament manufacture has been published by W. Dickie and P. Souter<sup>3</sup>. In the purification of ethylcellulose of 42-48% ethoxyl content<sup>4</sup>, the ether is dissolved in ligroin, hydrotoluene, cyclohexane or mixtures of them known by the trade-names "bornylan" (not bornyval which is ethyl isovalerianate) and "sangajol," being mixtures obtained from Borneo earth oil, heated and filtered while hot. Upon cooling the ethylcellulose separates out as a fine, flaky product, pure white in color.

A solution of methyl-, ethyl- or benzyl-cellulose in a solvent is formed into filaments by extrusion through orifices at the outlet of which the solution is received into a coagulating bath, the nature of the solvent being such, or the coagulation being carried out in such a way that a certain amount of the solvent remains. The threads are then heated and are obtained in a transparent, brilliant

1. Courtaulds, Ltd., and C. Diamond, E. P. 353597; abst. J. S. C. I. 1931, **50**, 921-B.

2. Deutsche Celluloid-Fabrik, E. P. 347423; abst. J. S. C. I. 1931, **50**, 672-B; Silk J. 1931, **3**, #89, 54. A. Weihe, O. Leuchs and E. Dörr, D. R. P. 528147; abst. C. A. 1931, **25**, 4705.

3. Textile Inst. J. 1931, **22**, 287-A.

4. E. Doerr, O. Leuchs, L. Rosenthal and I. G. Farbenindustrie, A.-G., U. S. P. 1814208; abst. C. A. 1931, **25**, 5287.

state<sup>1</sup>. Permanent plaited effects are obtained on fabrics consisting of thermoplastic methyl- or acetyl-cellulose<sup>2</sup> by passing them through a Chandler machine after being softened by impregnation or spraying with 25% aqueous solution of acetone. A cellulose ether or ester plasticizing agent has been patented<sup>3</sup>, consisting of an acidyl derivative of anisidine, acetyl-, butyryl- and propionyl-anisidine and -phenetidine or stearanilide being specified.

C. Dreyfus has devised a method of forming crepe fabrics of, or containing methyl- or benzylcellulose<sup>4</sup>, comprising weaving together ether filaments with degummed, undyed natural silk yarn, then subjecting the fabric to a creping bath. In stiffening a fabric containing cellulose ether filaments<sup>5</sup>, a softener is added in amount just sufficient to cause incipient coalescence of the filaments, at which point the solvent is removed by evaporation.

A novel textile material is formed by placing a sheet of cellulose ether high in plastificants in juxtaposition with a textile fabric<sup>6</sup>, and pressing with heat under such conditions that the sheet becomes plastic to the extent of causing adherence to the fabric. Artificial bristles, horsehair, straw, ribbons and similar heavy filaments are produced by extrusion of cellulose ether or ester solutions and incorporating with them by means of a harmonious solvent combination, benzene-, toluene- or xylene-sulfonamide-formaldehyde resin<sup>7</sup>. Fibers composed of cellulose ethers and esters are delustered, weighted or made resistant to hot ironing by treatment with colloidal solutions of inorganic substances (as aluminum, titanium, tin, silicon, zinc, cerium oxides,

1. C. Dreyfus, F. P. 697814; abst. C. A. 1931, **25**, 3168.

2. *Ibid.* U. S. P. 1793915; abst. J. S. C. I. 1931, **50**, 969-B.

3. *Ibid.* Can. P. 317329.

4. *Ibid.* U. S. P. 1813530; abst. C. A. 1931, **25**, 5301.

5. *Ibid.* U. S. P. 1828397.

6. *Ibid.* U. S. P. 1829983. Can. P. 315773.

7. C. Dreyfus and British Celanese, Ltd., E. P. 342340; abst. C. A. 1931, **25**, 5029. Cites E. P. 317456, 318630, 318631, 318643.

barium carbonate or sulfate, zinc sulfide or China clay) whereby absorption of these substances takes place<sup>1</sup>.

Fabrics containing cellulose ethers or esters may be simultaneously embossed and printed by wetting the fabric with a liquid capable of softening the cellulose derivative and also of at least partially dissolving the dyestuff to be used, then contacting the fabric with a transfer sheet containing the dyestuff dispersed in a wax by means of an embossing device<sup>2</sup>. Or<sup>3</sup>, the textiles may be dyed with vat dyes by applying the leuco compounds by means of a medium of relatively low alkali. Example, methylcellulose tissue is treated for 1 hr. at 75° with 5% Anthrene blue-green B, then with hydrosulfite and sodium carbonate and washed.

A reduced or modified luster may be obtained on cellulose ether filaments by adding to the solutions used for dry or wet spinning<sup>4</sup>, 0.5-2% of finely divided white pigment (barium, lead or calcium sulfate; zinc, calcium or magnesium carbonate; zinc oxide, aluminum oxide, barium phosphate or silica), and to minimize settling, materials of low specific gravity may be added as lithium or magnesium silicates in the presence of dispersing agents. Starch ethers may also be used. For the production of ornamental effects on mixed fibers, as of cotton and cellulose ethers<sup>5</sup>, the fabric is heated with a solution of a mineral acid or a salt having an acid reaction (aluminum or ferric chloride), the cellulose material being removed by washing or brushing, without drying in the presence of the carbonizing chemical.

1. C. Dreyfus, H. Platt, British Celanese, Ltd., and R. Parkinson, E. P. 343121; abst. J. S. C. I. 1931, **50**, 485-B; Silk J. 1931, **8**, #85, 53.

2. C. Dreyfus, W. Whitehead and H. Platt, U. S. P. 1825342.

3. C. Dreyfus, F. P. 698269; abst. C. A. 1931, **25**, 3176.

4. H. Dreyfus, E. P. 338490; abst. C. A. 1931, **25**, 2567; Chim. et Ind. 1931, **25**, 955.

5. *Ibid.* E. P. 339300; abst. J. S. C. I. 1931, **50**, 244-B. F. P. 698418; abst. C. A. 1931, **25**, 3177. Cites E. P. 260312, 302363.

In the fixation of luminous and phosphorescent substances on textiles containing cellulose ethers<sup>1</sup>, the application is made while the latter is in a swollen or softened state. The phosphorescent substances are applied locally as by printing or stencilling, or simultaneously with the softening agent. Ribbons and tapes of flattened cross-section of methyl-, ethyl- or benzyl-cellulose<sup>2</sup> are made by applying heat and pressure to filaments containing plasticizers, or to twisted or untwisted warps, or woven or knitted narrow strips of fabrics. Organic-soluble cellulose esters of hydroxycarboxylic acids or their derivatives, particularly cellulose glycollic acids<sup>3</sup>, are prepared by treating cellulose in stages with sufficient halogenated organic acid (chloracetic acid) to introduce more than one group into the cellulose molecule, the reaction being carried out in the presence of an amount of alkali hydroxide exceeding 3 times the weight of the water present, which should be 1.5-4 times the weight of the cellulose.

Metals may be incorporated with textiles containing cellulose ethers<sup>4</sup> by the use of white or colorless metal organic compounds (diethyl zinc, tetraethyl lead, zinc or aluminum ethylated, aluminum isopropylate, butylate, phenolate, *o*-cresolate, tetraethyl titanate, methylzinc methylate or ethylate) which are afterwards decomposed with precipitation of the metal in a very finely divided form. In the formation of nitrogen-containing aralkyl cellulose ethers<sup>5</sup>, compounds have been described using as etherifying agents, nitrobenzyl chloride, *p*-nitrophenylethyl chloride, 2-nitro-

1. H. Dreyfus, E. P. 340636; abst. Silk J. 1931, **7**, #83, 54.

2. *Ibid.* E. P. 341034; abst. C. A. 1931, **25**, 4720; Silk J. 1931, **7**, #84, 53. F. P. 702209, 702210; abst. C. A. 1931, **25**, 4125. Compare E. P. 248147, 249946, 328312. See also F. P. 700876, 701269; abst. C. A. 1931, **25**, 3833.

3. *Ibid.* E. P. 343521; abst. C. A. 1931, **25**, 5557; J. S. C. I. 1931, **50**, 480-B; Silk J. 1931, **8**, #85, 54; Brit. Plastics, 1931, **3**, #28, 63. F. P. 703650; abst. C. A. 1931, **25**, 4705.

4. *Ibid.* E. P. 343949; abst. C. A. 1931, **25**, #17, 4719; J. S. C. I. 1931, **50**, 486-B. F. P. 702210.

5. *Ibid.* E. P. 344420; abst. J. S. C. I. 1931, **50**, 626-B; Silk J. 1931, **8**, #86, 54. See E. P. 164375.

1,4-dichlormethylbenzene, 2-chlormethylbenzylamine, *o*-chlorpropylaniline, and 3-acetaminobenzyl chloride, producing nitrobenzylcellulose, nitrophenylethylcellulose, nitrodichlormethylcellulose, chlormethylbenzylcellulose and acetaminobenzylcellulose as examples. These bodies are stable, soluble in acetic acid and other solvents and have an affinity for acid dyestuffs.

When cellulose esters (glycollate, malonate, maleate, phthalate, malate, oxalate) are treated with thionyl chloride in an excess of aniline<sup>1</sup>, new nitrogen-containing cellulose ethers result which have affinity for wool dyes. Cellulose ethers or esters may be produced containing the nitrile group -CN as chloracetonitrile, cyanacetyl chloride, or *a*-, or *b*-chlorpropionitrile by acting as etherifying agents upon alkalicellulose. The products are soluble in acetic acid, tetrachlorethane, insoluble in alcohol, ether and water<sup>2</sup>. Yarns containing cellulose ether filaments may be reduced in luster by adding thereto in a very finely divided condition, cotton flock or subdivided rayon filaments<sup>3</sup>. A process for the manufacture of halogen-containing cellulose ethers comprises reacting upon a carboxy ester (cellulose malonate, malate, maleate, oxalate, phthalate) or hydroxy ether (cellulose glycollate) with thionyl chloride dissolved in benzene at 25-35°, removing excess of reactants under vacuum, and precipitating the cellulose ether<sup>4</sup>. Cellulose derivatives containing nitrogen are produced from cellulose material pretreated with mineral or organic acids or alkalis, from incompletely etherified celluloses by treatment with primary or secondary amines at 150-200° under pressure<sup>5</sup>. Methylamine, dimethylamine, ethylamine, diethylamine,

1. H. Dreyfus, E. P. 344480; abst. J. S. C. I. 1931, **50**, 626-B; Silk J. 1931, **8**, #86, 53. F. P. 704280; abst. C. A. 1931, **25**, 4705.

2. *Ibid.* E. P. 344488; abst. J. S. C. I. 1931, **50**, 626-B. F. P. 704871; abst. C. A. 1931, **25**, 4705.

3. *Ibid.* E. P. 344510; abst. Silk J. 1931, **8**, #86, 54.

4. *Ibid.* E. P. 344529; abst. J. S. C. I. 1931, **50**, 626-B. F. P. 704872.

5. *Ibid.* E. P. 345989; abst. J. S. C. I. 1931, **50**, 626-B; Silk J. 1931, **8**, #87, 54.

methylaniline, tri- or tetra-methylammonium iodide or methyltriethylammonium iodide are particularly suitable, the final cellulose products having an affinity for acid dye-stuffs.

H. Dreyfus<sup>1</sup> prepares artificial filaments of cellulose ethers by incorporating in the spinning solution prior to filament formation finely divided natural or synthetic resins of melting point above 250°, and which are insoluble in the usual solvents, the resin being in a very fine state of dispersion. Etherified celluloses are formed by treating alkali-cellulose with an aliphatic etherifying agent containing a halogen atom in addition to the etherifying group (epichlorhydrin), or with one containing halogen atoms of different reactivity, so that halogen is retained in the product (ethylene monochlorbromide). The halogen substituted derivatives are then reacted upon with ammonia or amines to yield cellulose amido-ethers having an affinity for acid dyes and being soluble in chloroform-alcohol<sup>2</sup>. H. Dreyfus has described a process for sizing and finishing threads and textiles by the application thereto of a solution or aqueous dispersion of cellulose ether<sup>3</sup>.

Organic substances are added to cellulose ether and ester filaments to reduce or modify their luster, being incorporated in the solution used for filament formation. Examples are, diacetylbenzidine, dibenzoylbenzidine, diacetyl-tolidine, thiocarbobenzidine, 4,4'-diureidobiphenyl, 4,4'-di-thioureidobiphenyl and  $\alpha$ -dinaphthylurea. The size of the particles, if not in solution, is about 0.5 micron<sup>4</sup>. In another method of delustering<sup>5</sup>, suspensions, dispersions or colloidal solutions of titanium dioxide, aluminum oxide,

1. H. Dreyfus, E. P. 346793. Can. P. 315360. Cites E. P. 346678.

2. *Ibid.* E. P. 346806; abst. J. S. C. I. 1931, **50**, 626-B. Can. P. 311408.

3. *Ibid.* F. P. 700711; abst. C. A. 1931, **25**, 3848. Cites F. P. 574947.

4. *Ibid.* F. P. 702174; abst. C. A. 1931, **25**, 4125. Cf. F. P. 686330, 688625.

5. *Ibid.* F. P. 703626; abst. C. A. 1931, **25**, 4402.



kaolin or bentonite are used, swelling agents being applied at the same time to facilitate absorption. In producing specific effects on acetate or ether textiles and fibers<sup>1</sup>, a paste of acacia, a dye (Auramine or Malachite green), stannous chloride, potassium thiocyanate and citric acid is applied either evenly or intermittently over the surface, and then submitted to a steaming operation.

For the direct dyeing of cellulose ethers in a neutral or weakly acid bath<sup>2</sup>, compounds as 4-aminobenzyl-*w*-sulfonic acid, ammonium 5-nitro-2-aminobenzyl-*w*-sulfonate or 3-5-dinitro-2-aminobenzyl-*w*-sulfonic acid are diazotized and coupled with components as methylbenzylaniline, ethylbenzylaniline, methyl-2-naphthylamine, methyldiphenylamine, ethyl-2-naphthylamine or 2-naphthylamine, producing yellow, orange and red colorings. In the manufacture of aliphatic acids, either free or in the ester form<sup>3</sup>, alkyl ethers are caused to react with carbon monoxide in presence of a catalyst capable of forming acetic acid or acetates by reaction with CO, such as alkali alcoholates (sodium methylate or ethylate) or alkali formates (potassium or sodium). Alkyl ethers (dimethyl ether, diethyl ether) may be similarly formed<sup>4</sup>.

An apparatus has been described for cellulose ether artificial filament manufacture<sup>5</sup>, in which the solution is extruded or spun into a closed chamber, such as the cells or compartments of a dry spinning metier of the cellular type (wherein a metier casing is subdivided into individual spinning cells by partitions) and through which passes a heated evaporative medium as air. A process for dyeing methyl- or ethyl-cellulose has been patented<sup>6</sup>, which comprises a loading operation wherein the material is swollen and im-

1. H. Dreyfus, E. P. 702353. Compare F. P. 692734.
2. W. Duisberg, W. Hentrich and L. Zeh, U. S. P. 1757419; abst. C. A. 1930, **24**, 3379. Cites D. R. P. 141783, 442310.
3. H. Dreyfus, Can. P. 305320.
4. *Ibid.* Can. P. 305321.
5. H. Dreyfus, E. Kinsella, J. Bower and W. Taylor, U. S. P. 1814468. Compare U. S. P. 1541104, 1602125.
6. H. Dreyfus, U. S. P. 1805467; abst. C. A. 1931, **25**, 3847.

pregnated with a salt of a loading material and the metal then fixed in the compound in an insoluble condition, stannic chloride followed by disodium phosphate being an example.

In the formation of plastic cellulose ether or ester masses<sup>1</sup>, instead of using high boiling plasticizers or difficulty dissolving fluids which require a comparatively long period for their removal in the seasoning operation of celluloids manufacture, A. Eichengruen has found that by the use of swelling agents which have no solvent effect upon the cellulose compound, moldable articles may be fabricated in much less time due to greater facility of removal of *swelling* agent in contradistinction to *dissolving* agent. Fast dyeings on cellulose ethers with basic monoazo dyestuffs result by the use of a dye of the type produced from diazotized 4-aminobenzene-1-sulfamide and aminocresol ether, or diazotized 2-nitro-1-aminobenzene-4-sulfamide and naphthylamine, golden yellow, orange and reddish-orange shades being produced<sup>2</sup>.

In making films of great length from cellulose derivatives<sup>3</sup>, a layer is formed of the cellulose, then a metallic surface formed on the layer whereby the static electricity engendered or received is drawn from the surface. A thin film of about 0.01 mm. thickness is first formed, dried, and an ethylcellulose support superposed on this, but after the application of each layer, superficial reduction of the same is resorted to<sup>4</sup>. "Genuine" methylglycol lignin (methylin) may be prepared in about 70% yield by Soxhlet of pine wood sawdust with boiling methylglycol in presence of HCl. The product is a light, easily filterable powder, soluble in methylglycol, pyridine, acetic acid and dilute alkali, partly soluble

1. A. Eichengruen, Swiss P. 143406. Mentions D. R. P. 238348, 395083, 395084, 395104, 441023, 445308, 452910.

2. H. Eichwede and E. Fischer, U. S. P. 1802204; abst. C. A. 1931, **25**, 3497.

3. G. Frenkel, F. P. 698800; abst. C. A. 1931, **25**, 3482.

4. *Ibid.* F. P. 698801; abst. C. A. 1931, **25**, 3482.

in warm ether, acetone and chloroform<sup>1</sup>. H. Gardner<sup>2</sup> produces a radio-active luminous cellulose ether filament by admixing with the cellulose derivative in solution before spinning, titanium oxide that has previously been treated with radium bromide. Organic dyestuffs may be added to impart various colors.

In the production of regular pattern multicolor screens by means of dye-repellent resists<sup>3</sup>, the dyes in a non-penetrative condition or medium, are applied to intermediate surface layers of a film support of cellulose ether or ester; e.g., a powdered dye as cochineal is suspended in a viscous liquid as castor oil, and this added in the proportion desired. L. Goodman<sup>4</sup> prepares translucent sheets or films by taking Yoshino paper such as used for stencil manufacture, and impregnates with a solution of a cellulose ether or ester with plasticizing agents added, the skin, when dry, being used as a wrapper for meat products as sausage. In the preparation of mixed cellulose ether-esters, cotton, or partially acetylated cellulose, is treated with a nitrated benzyl-halide (nitroxylyl chloride, *o*- or *p*-nitrochlorbenzene, 1-chlor-2,4-dinitrobenzene), thus producing a diazotizable fiber, an example of the finished product being nitroxylyl-cellulose<sup>5</sup>.

In an investigation of the reactivity of methylated sugars, C. Gross and W. Lewis<sup>6</sup> report that the equilibrium solution from xylose and dilute calcium hydroxide contains xylose, lyxose and a condensation product derived from 4 mols. of the expected 2-ketoxxylose. Similarly, 2,3,4-trimethylxylose yields trimethyllyxose. In a dissertation on

1. W. Fuchs and R. Daur, *Cellulosechemie*, 1931, **12**, 103; abst. C. A. 1931, **25**, 5761.
2. U. S. P. 1791199; abst. *Chem. et Ind.* 1931, **25**, 1217.
3. J. Goldsmith, T. Baker, C. Bonamico and Spicers, Ltd., E. P. 339238; abst. C. A. 1931, **25**, 2378. Cites E. P. 225659, 333865, 334265.
4. L. Goodman, U. S. P. 1829702. F. P. 717453. Mex. P. 32718. Belg. P. 380037. P. Klason, *Svensk Papper, Tid.* 1924, **27**, 261.
5. C. Graenacher, E. P. 347117; abst. *Textile Mfr.* 1931, **57**, 306. E. P. 346385.
6. J. A. C. S. 1931, **53**, 2772; abst. C. A. 1931, **25**, 4230; J. S. C. I. 1931, **50**, 1037-A.

the solubility and physical strength of cellulose derivatives in relation to constitution, M. Hagedorn and P. Möller<sup>1</sup> find that with the cellulose ethers, water resistance increases in direct ratio with carbon content. They have prepared a table showing the solubility of methyl-, ethyl-, propyl-, butyl-, benzyl-, ethylbutyl-, ethylbenzyl-, propylbenzyl-, and butylbenzyl-cellulose in water, alcohol, ether, acetone, ethyl acetate, benzene, benzene and chlorinated hydrocarbons. In the production of aminocellulose derivatives<sup>2</sup>, alkalicellulose is esterified with benzene- or toluene-sulfonyl chloride, and then acetylated or alkylated, and finally treated with a primary, secondary or tertiary amine. The "animalized cellulose" thus obtained, as also its mixtures with ordinary cellulose esters or ethers, has affinity for acid dyes. Suitable amines are aniline, diethylamine, pyridine and *iso*amylamine.

In the preparation of cellulose esters in which the esterified body does not pass into solution, cellulose or partially etherified cellulose is treated with chlorobenzene (or chlornaphthalene) with pyridine and acetyl chloride (or propionyl chloride, crotonyl chloride), the product being soluble in chlormethane, tetrachlorethane and chlorethane, methanol<sup>3</sup>. Cellulose formate may be substituted for cotton as initial material. In the F. Hahn process for cellulose etherification<sup>4</sup>, cellulose is ground and then added to a slurry of alkali in an inert medium (benzene) and after intimate admixture etherification is effected by the addition of methyl or ethyl chlorides under pressure. The C. Palmer method of simultaneous production of filaments of cellulose ethers or esters and of threads of other fibers<sup>5</sup>, comprises

1. Cellulosechem. 1931, **12**, 29; abst. J. S. C. I. 1931, **50**, 436-B; Brit. Plastics, 1931, **3**, #28, 180; Nitrocellulose, 1931, **2**, 39.

2. M. Hagedorn, A. Ossenbrunner and I. G. Farbenindustrie, U. S. P. 1833286. E. P. 279801.

3. M. Hagedorn and O. Reichert, U. S. P. 1822381.

4. U. S. P. 1819600; abst. C. A. 1931, **25**, 5769. U. S. P. 1501207.

5. U. S. P. 1672083; abst. C. A. 1928, **22**, 2669; Rayon, 1928, **7**, #1, 17.

forming dry spun filaments of cellulose derivatives in a metier casing, withdrawing the filaments directly from the casing and feeding them into intimate association with the filaments to be attached thereto or incorporated therewith, at the same time inducing a twisting and winding motion to bring the dissimilar filaments into more intimate contact.

Cellulose compounds derived from cyanogen halides (chloride or bromide) are obtained by treating alkalicellulose with halogen halide in the presence of an indifferent solvent (ether, carbon tetrachloride), the product obtained appearing similar to cotton but containing 1.7-1.9% nitrogen and being capable of taking acid wool dyestuffs in strong shades<sup>1</sup>. Polychromatic reserves for fabric printing are produced by using ester salts of leuco compounds of vat dyes with a thickening agent which has a reserve action in the final alkali vat<sup>2</sup>. The printing material advocated contains sodium leucoindigosulfonate, *α*-methylcellulose, ammonium oxalate, sodium chlorate and ammonium vanadate.

Incidental to an investigation of the structure of carbohydrates and their optical rotatory power, W. Haworth, E. Hirst and H. Streight<sup>3</sup> have described the methylation of 4-*b*-glucosido-*α*-methylmannoside and 4-*b*-glucosidomannonic acid, and the hydrolysis of heptamethyl-4-*b*-glucosido-*α*-methylmannoside and methyloctamethyl-4-*b*-glucosidemannonate. Also<sup>4</sup>, methylation of 4-*b*-galactosido-*α*-mannoside and 4-*b*-galactosidomannonic acid, and the hydrolysis of heptamethyl-4-*b*-galactosido-*α*-methylmannoside.

Acetone-soluble cellulose acetate can be completely methylated by treatment with methyl sulfate and 30% NaOH in acetone at 55°. Acetolysis of trimethylcellulose at 15° followed by simultaneous deacetylation and methylation, yields tetramethylglucoside (15%), heptamethyl-*b*-methylcellotri- (18%) and decamethyl-*b*-methylcellotri-

1. J. Haller, U. S. P. 1813619.
2. G. Hasse, D. R. P. 519984; abst. C. A. 1931, **25**, 3497. See also D. R. P. 418487, 433146.
3. J. C. S. 1931, **137**, 1349.
4. W. Haworth, E. Hirst and M. Plant, J. C. S. 1931, **137**, 1354.

oxide. From the residue is obtained a methylated cellodextrin<sup>1</sup>. Derivatives of *d*-glucose-6-methyl ether have been described<sup>2</sup>, and the synthesis of 5-methylketose<sup>3</sup>. R. Herzog and B. Lange<sup>4</sup> have reported on an optical method which makes possible the determination of the colloidal phase from the state of polarization of the Tyndall change. On carefully made preparations of methyl- and acetyl-cellulose in chloroform and tetrachlorethane, a change in state of dispersion with time can be estimated. This change, especially at higher temperatures and great dilutions, is extensive, and becomes stationary only after several days.

Cellulose may be converted into a loose, finely dispersed form easily etherified mass by distributing the cellulose in the presence of water in a high boiling diluent as dichlorobenzene, anisol, benzyl chloride, dimethylaniline, diethyl-*p*-toluidine or ethylbenzylaniline<sup>5</sup>. Deep greenish-yellow tints are produced on cellulose ether or ester silk by the use of compounds which are non-sulfonated in the nucleus, such as are obtainable by interaction of 4-amino-1.8-naphthalic anhydride with hydrazine or phenylhydrazine<sup>6</sup>. In producing a photographic roll film<sup>7</sup>, the sensitive layer with a protective paper backing is covered with transparent foil of cellulose ether or ether-ester, colored to serve as a light filter when the film is exposed. In preparing ethers of cellulose or starch<sup>8</sup>, the reaction is carried out under

1. W. Haworth, E. Hirst and H. Thomas, J. C. S. 1931, **137**, 821; abst. C. A. 1931, **25**, 3828; J. S. C. I. 1931, **50**, 941-A.

2. B. Helferich and E. Guenther, Ber. 1931, **64-B**, 1276; abst. C. A. 1931, **25**, 4230.

3. E. Hersant and W. Linnell, Quart. J. Pharm. Pharmacol. 1931, **4**, 52; abst. C. A. 1931, **25**, 5402.

4. Proc. World Eng. Cong., Tokyo, 1931, **31**, 501; abst. C. A. 1931, **25**, 5554.

5. E. Huber, U. S. P. 1805365; abst. C. A. 1931, **25**, 3832.

6. I. G. Farbenindustrie, Akt.-Ges., E. P. 338095, Addn. to 304739; abst. C. A. 1931, **25**, 2303; J. S. C. I. 1931, **50**, 243-B. W. Eckert, C. Muller and W. Gmelin and I. G. Farbenind., A.-G., D. R. P. 516982, Addn. to 515029; abst. C. A. 1931, **25**, 2007.

7. *Ibid.* E. P. 338741; abst. C. A. 1931, **25**, 2379.

8. *Ibid.* F. P. 656861; abst. C. A. 1929, **23**, 4342.

vacuum and in the presence of a gas as CO<sub>2</sub>, which is afterwards absorbed by the NaOH used.

Azo dyes insoluble in water are made in substance or on a sub-stratum of cellulose ether or ester<sup>1</sup>, by coupling a diazo, tetrazo or diazoazo compound free from carboxyl, sulfonic and hydroxyl groups with an arylide such as 2'.3'-hydroxynaphthoyl-4-amino-1.2-dimethoxybenzene (which may be made from 2.3-hydroxynaphthoic acid and the corresponding 4-amino-1-alkoxymethoxybenzene). Cellulose ethers may also be dyed with monazo dyes prepared by combining diazotized aromatic compounds with phenol or its derivatives<sup>2</sup>, the positions *p*- to the OH groups of which are free, and which contain no other substituents than alkyl radicals, and treating, if desired, with alkyl halides or acid chlorides. Example, monoacetyl-*p*-phenylenediamine with *o*-cresol. Cellulose ether or ester lacquers are colored with the calcium salts of sulfonated azo dyes of the type; nitro-arylamine + acetoacetic arylamide<sup>3</sup>, examples being acetoacetic sulfo-*o*-anisidine coupled with diazotized 5-nitroanthranilic acid, *o*-nitroaniline or 5-nitro-*o*-toluidine-*w*-sulfonic acid. These lacquers are said to be excellent for application to leather or metal.

Stains of copying inks or pencils or from typewriter ribbons may be removed by the use of compositions of pasty consistency containing a cellulose ether swollen by water, such as methylcellulose or cellulose glycollic acid, with or without the addition of soap and glycerol<sup>4</sup>. In artificial filament formation in order to obtain the orientation of the micellae desired<sup>5</sup>, the spinning solution is extruded into a chamber which has been freed by air and saturated with the vapor of a swelling agent for the cellulose derivative. A binding material for bleaching-out layers comprises one

1. I. G. Farbenindustrie, E. P. 339620; abst. C. A. 1931, **25**, 2855.

2. *Ibid.* F. P. 700239; abst. C. A. 1931, **25**, 3847.

3. *Ibid.* E. P. 339936; abst. J. S. C. I. 1931, **50**, 351-B.

4. *Ibid.* E. P. 340232; abst. C. A. 1931, **25**, 4097.

5. *Ibid.* E. P. 340570; abst. Silk J. 1931, **7**, #83, 52. E. P. 327420.

component which is capable of retaining the dyestuff in solution and one which swells in the fixing agent and in which the dyestuff is insoluble<sup>1</sup>. Examples of the first component are alcohols of high boiling point, cellulose esters and softening agents, such as those used for photographic films, and of the second component cellulose ethers and ether-esters. Example, a mixture of ethylbenzylcellulose and nitrocellulose is sensitized with diethylthiosinamine, the fixing agent being a mixture of benzine and anisole.

Cellulose acetate filaments are sized by means of a water-soluble hydroxyalkylether of a carbohydrate obtainable by reacting on a carbohydrate with an alkylene oxide in the presence of aqueous alkali<sup>2</sup>. Example, cellulose acetate silk is immersed in hydroxypropyl starch or hydroxypropylcellulose, the size being afterwards removed by agitating in water at 60° without further additions. Lacquer coatings, films, and artificial threads are formed of<sup>3</sup> butyl- or benzyl-cellulose combined with substituted guanidines or aralkylated organic bases (triphenylguanidine, biguanides, *b*-naphthylbiguanide, benzyl- and dibenzyl-aniline, carbazole, *N*-ethylcarbazole). It is claimed that films made from benzylcellulose 20, naphthylbiguanide 0.4-0.5, last approximately five times as long as corresponding benzylcellulose films free from base. Fabrics which have been mercerized, and then had applied thereto a cellulose ether lacquer<sup>4</sup> are said to show excellent dielectric properties when used for insulating purposes.

Straw, sea-weed, esparto grass, wheat-, rye- and barley-straw, containing fibers which are encrusted but not turned into wood, may be alkylated and especially benzylation by the methods used for making cellulose ethers, the products being soluble in chloroform, benzyl alcohol, ben-

1. I. G. Farbenindustrie, E. P. 341151.

2. *Ibid.* E. P. 341516; abst. C. A. 1931, **25**, 4720; J. S. C. I. 1931, **50**, 486-B; Silk J. 1931, **7**, #84, 54.

3. *Ibid.* E. P. 342288; abst. C. A. 1931, **25**, 4725; J. S. C. I. 1931, **50**, 404-B; Brit. Plastics, 1931, **3**, #26, 44.

4. *Ibid.* E. P. 342848.



zene, toluene, pyridine and trichlorethylene<sup>1</sup>. A layer for use in the bleach-out process<sup>2</sup> comprises a nitrogen-free, basic oxonium dyestuff other than a xanthocyanin. Such dyestuffs are, for example, 3-6-dihydroxy-9-phenylxanthoxonium chloride and its ethers and 3,6-dimethoxy-9-*o*-carbmethoxyphenylxanthoxonium chloride. A layer for the production of multicolor pictures comprises a mixture of resorcinbenzeindimethyl ether bromide, anilinodimethylaminophenonaphthoxyzine chloride and 2,7-dimethyl-3-dimethylamino-6-methylaminoazononium phenyl chloride in a mixture of ethylcellulose butyrate and nitrocellulose.

Lacquers are formed by combining a synthetic resin of urea, methylurea or its anhydride with formaldehyde type and in an exceedingly fine state of subdivision<sup>3</sup>, with cellulose ethers dissolved in cyclohexanone, paraldehyde, dimethylacetal, diethylacetal, anisole, aniline, pyridine or 1,4-dioxane. Primary oxyalkylcellulose acetates soluble in acetone are prepared by acetylating monohydroxyalkylcelluloses (oxyalkylcelluloses) with acetic anhydride, acetic acid and a catalyst at a temperature below that at which hydrolysis takes place. Benzyloxycellulose, benzyloxybutylcellulose and propyloxyethylcellulose are examples. The ethers are soluble in benzene<sup>4</sup>. The luster of cellulose ether or ester yarns and fabrics is reduced by impregnating with a solution of urea, drying, steaming 20-30 minutes and drying. The effect of the urea may be increased by adding water-soluble aliphatic hydroxycarboxylic acids (glycollic or lactic) or their sodium salts<sup>5</sup>. Esters of cellulose or other carbohydrates are prepared by first partially substituting by an alkoxy compound the OH group of the carbohydrate

1. I. G. Farbenindustrie, E. P. 343147; abst. C. A. 1931, **25**, 5557; J. S. C. I. 1931, **50**, 582-B.

2. *Ibid.* E. P. 343212.

3. *Ibid.* E. P. 344626; abst. C. A. 1931, **25**, 4725. Cites E. P. 327673.

4. *Ibid.* E. P. 345028; abst. J. S. C. I. 1931, **50**, 672-B. F. P. 698392; abst. C. A. 1931, **25**, 3167. Compare D. R. P. 363192, F. P. 650973.

5. *Ibid.* E. P. 345673, Addn. to 309194; abst. J. S. C. I. 1931, **50**, 534-B; Textile Mfr. 1931, **57**, 304; Silk J. 1931, **8**, #87, 54.

and afterwards esterifying the alkoxy compound<sup>1</sup>. Thus, cellulose treated with ethylene oxide and afterwards esterified to give a mixed aceticbutyric ester of a partially hydroxyethylated cellulose (hydroxyethylcellulose acetobutyrate) is directly soluble in acetone. A desirable lacquer is said to result<sup>2</sup> when ethylcellulose insoluble in water 1 is dissolved in carbon tetrachloride and methylene chloride 5 each with the addition of ethyl alcohol 0.5-1.

Cellulose, cellulose hydrate or hydrocellulose is etherified in one stage with caustic soda solution and an etherifying agent in the presence of solid NaOH, a non-reactive salt (sodium chloride, see p. 98 and 000), and an indifferent solvent or diluent (benzene), the weight of the water present in the reaction mixture not exceeding that of the cellulose<sup>3</sup>. Mixed ethers or ether-esters of cellulose, especially esters of low molecular weight (cellulose acetobutyrate) are plasticized by beating up or rolling the cellulose derivative with substances exerting a swelling action upon the cellulose when heated<sup>4</sup>. Example, oxyethylcellulose acetate 10, *p*-toluenesulfamide 2, lithopone 5, ethyl alcohol 1 are calendered, and the intumesced mass thus formed directly molded. With cellulose tripropionate, chlortoluene (benzyl chloride) is recommended.

Cellulose ether and ester silk may be dyed with an aryliide of 2,3-hydroxynaphthoic acid mixed with a solvent of the cellulose derivative, only sufficient solvent being used to swell the cellulose compound<sup>5</sup>. Examples, 2,3-hydroxynaphthoyl-2'-toluidine with 4'-methoxydiphenylamine-4-diazonium chloride, intense blue. 2,3-Naphthoic acid anilide with diazotized 3-chloraniline, brilliant orange. 2,3-Hydroxynaphthoyl-2'-anisidine with 4'-methoxydiphenylamine-4-

1. I. G. Farbenindustrie, F. P. 695283; abst. C. A. 1931, **25**, 2847.

2. *Ibid.* E. P. 346040; abst. J. S. C. I. 1931, **50**, 643-B.

3. *Ibid.* E. P. 346426; abst. J. S. C. I. 1931, **50**, 671-B; Silk J. 1931, **8**, #88, 54.

4. *Ibid.* F. P. 704862; abst. C. A. 1931, **25**, 4673.

5. *Ibid.* E. P. 348269. Cites E. P. 195619, 224502, 241854. D. R. P. 346883.

diazonium chloride, reddish-blue. In the manufacture of dyes, and dyeing cellulose ethers and esters<sup>1</sup>, aminoanthraquinonecarboxylic amides containing a second auxochromic group are synthesized, and give blue shades. Example, 1-aminoanthraquinone-2-carboxylamide condensed with formaldehyde, nitrated, and the nitro-compound reduced to 1-4-diaminoanthraquinone-2-carboxylamide, gives blue. Prints obtained from vat dyes with the aid of methylcellulose<sup>2</sup> are fixed, without steaming, by means of a salt bath containing alkali and a reducing agent (hyposulfite). Masses or objects may be prepared partly or wholly of aqueous soluble methylcellulose<sup>3</sup>, by pressing layers or plates of the ether on one another with simultaneous treatment with water or aqueous solutions, thus obviating the use of expensive volatile solvents.

Cellulose ethers or esters may be colored by incorporating into them chromium or copper compounds of dyes<sup>4</sup>, particularly *o*-hydroxyazo dyes. Examples, alcohol-benzene soluble ethylcellulose 15, ethyl alcohol and benzene 100 each, castor oil 1 is admixed, and 2 parts of the chromium compound added of the diazotized 5-nitro-2-amino-1-oxybenzene and 1-phenyl-3-methyl-5-pyrazolon, pure red being formed. Methyl- or benzyl-cellulose react similarly. In delustering fabrics of regenerated cellulose<sup>5</sup>, the material is treated with a cellulose ether or ester in conjunction with a non-solvent of it, a cloudy film being produced on the material when dry. Example, benzylethylcellulose

1. I. G. Farbenindustrie, E. P. 350928; abst. J. S. C. I. 1931, **50**, 1004-B.

2. I. G. Farbenindustrie, Akt.-Ges., A. Schmidt and E. Pfeffer, D. R. P. 515305; abst. C. A. 1931, **25**, 2007; Kunst. 1931, **21**, 94. D. R. P. 155415, 193121, 239094, 448286.

3. I. G. Farbenindustrie, Akt.-Ges., G. Balle and K. Sponsel, D. R. P. 516751; abst. C. A. 1931, **25**, 3167.

4. I. G. Farbenindustrie, Akt.-Ges., W. Mueller, K. Holzach and H. Krzikalla, D. R. P. 517491; abst. C. A. 1931, **25**, 2304. Cites D. R. P. 337993.

5. I. G. Farbenindustrie, Akt.-Ges., W. Schieber, H. Pfannenstiel and H. Mahn, D. R. P. 518194; abst. C. A. 1931, **25**, 2577. I. G. Farbenindustrie, Akt.-Ges., G. Poetzsch and H. Jaeger, D. R. P. 518197; abst. C. A. 1931, **25**, 2576. I. G. Farbenindustrie, Akt.-Ges., K. Sponsel and G. Balle, D. R. P. 518241; abst. C. A. 1931, **25**, 3481.

in equal parts of methyl alcohol and benzene to which 10% water has been added. In producing paper glazed on one side only<sup>1</sup>, the side to be glazed is moistened with dimethyl-cellulose solution before pressing.

As an electrical insulating composition<sup>2</sup>, mixtures of cellulose esters of higher fatty acids or cellulose ethers containing higher fatty acid radicals (above C<sub>10</sub> atoms) are recommended. To produce a mat effect on textiles, paper or other objects containing cellulose ethers<sup>3</sup>, the latter are dissolved in glycollic or lactic acids or their sodium salts with urea and volatile solvents and one or more coatings applied. A desirable solvent combination for triethylcellulose or cellulose dinaphthenate, naphthenate-laurate, acetobutyro-laurate, butyro-laurate or laurate is carbon bisulfide 92, benzene 8, or carbon bisulfide 96, acetone 4, transparent solutions resulting<sup>4</sup>. As a size for acetate silk<sup>5</sup>, hydroxyalkyl carbohydrates (oxyethylcellulose, oxypropyl starch, oxybutyl starch) has received patent protection. When moistened alkalicellulose is treated with a gaseous etherifying agent under pressure with temperature regulating means at about 70°, the corresponding cellulose ether is obtained in nearly theoretical yield<sup>6</sup>. Methyl chloride, ethyl chloride or mixed methyl-benzyl chlorides produce the corresponding methyl-, ethyl- and methylbenzyl-celluloses, the latter containing 24.7% methoxyl and 8% benzyl in cellulose combination. When alkalicellulose is treated with a mixture of ethyl and benzyl chlorides, ethylbenzylcellulose results, being a monoethylcellulose containing 1%

1. I. G. Farbenindustrie, Akt.-Ges., K. Franz and C. Dankert, D. R. P. 518724; abst. C. A. 1931, **25**, 3484.

2. I. G. Farbenindustrie, Akt.-Ges., and M. Hagedorn, D. R. P. 519457; abst. C. A. 1931, **25**, 2787.

3. I. G. Farbenindustrie, Akt.-Ges., A. Baumert and R. Fischer, D. R. P. 519983.

4. I. G. Farbenindustrie, Akt.-Ges., and A. Kaempff, D. R. P. 520411; abst. C. A. 1931, **25**, 2850.

5. I. G. Farbenindustrie, Akt.-Ges., M. Hagedorn and H. Gensel, D. R. P. 523434; abst. C. A. 1931, **25**, 3498.

6. I. G. Farbenindustrie, Akt.-Ges., O. Ernst and K. Sponsel, D. R. P. 522575; abst. C. A. 1931, **25**, 3832; Nitrocellulose, 1931, **2**, #4, 83.

benzyl, which may be acetylated in the usual manner to ethylcellulose acetate or ethylbenzylcellulose acetate<sup>1</sup>. Methyl or ethyl chloride with brombenzyl chloride gives rise to methyl- or ethyl-brombenzylcellulose which may likewise be esterified to an acetic ester.

Cellulose ethers insensitive to water (and this is the class of ethers of greatest technical value)<sup>2</sup>, result by treating metal compounds of cellulose (alkalicellulose) with an excess of etherifying agent containing up to 2 mols. of an aralkyl halide for each 10-30 mols. alkylating agent. The reaction is effected under such conditions of temperature and pressure that saponification of the excess of alkylating agent is avoided. Thus, alkalicellulose heated with ethyl chloride 14 and benzyl chloride 1 mol. to 110-120° in a pressure vessel produces ethylbenzylcellulose giving a clear solution in a mixture of equal volumes of alcohol-benzene, and substantially unaffected by water. In order to facilitate penetration of a dyestuff<sup>3</sup>, insoluble or difficultly soluble dyes are admixed with a small amount of methylcellulose before reducing the dye to small particles. Example, methylcellulose is added to a sodium hydroxide solution of 2-hydroxy-3-naphthoic acid anilide, and the whole added to acetic acid in ice water, a fine suspension resulting. A diazo solution may then be added. Or<sup>4</sup>, the material to be dyed is impregnated with an arylide of 2-hydroxy-3-naphthoic acid in an alkaline bath containing a small quantity of a water-soluble organic liquid that is a solvent or swelling agent for the cellulose ether or ester and is capable of dissolving the arylide. Pyridine, ethyl alcohol and acetone are

1. I. G. Farbenindustrie, Akt.-Ges., and E. Teupel, D. R. P., 521721; abst. C. A. 1931, **25**, 3481. U. S. P. 1833270.

2. I. G. Farbenindustrie, Akt.-Ges., G. Balle and K. Ost, D. R. P. 522054; abst. C. A. 1931, **25**, 3167.

3. I. G. Farbenindustrie, Akt.-Ges., F. Risse and E. Fischer, D. R. P. 523910.

4. I. G. Farbenindustrie, Akt.-Ges., W. Kirst and P. Sommer, D. R. P. 524350; abst. C. A. 1931, **25**, 3847. Cites D. R. P. 261594, 285664.

suitable organic liquids. After impregnation the materials are treated with a diazo compound to develop the color.

Coagulation of cellulose alkyl ethers (methylcellulose) of technical usefulness is prevented at high temperatures by addition of organic solvents containing the OH group which are wholly or partially miscible with water (methyl alcohol, propyl alcohol, glycol, glycerol, methyl glycol, acetol)<sup>1</sup>. A method of printing with vat dyes has been developed<sup>2</sup>, comprising mixing the dyes with methylcellulose before printing, and then treating the fabric with a reducing agent and alkali after printing. In the production of lacquers and other solutions from mixed cellulose ethers (methylpropyl-, ethylpropyl-, methylbutyl- and ethylbutylcellulose)<sup>3</sup>, the solvents recommended are mixtures of aliphatic or hydroaromatic hydrocarbons and alcohols, glycol-monomethyl (or ethyl or butyl) ether, cyclohexanol or methylglycol acetate. In producing cellulose ethers by treating moistened alkal cellulose with gaseous alkylating agents (methyl or ethyl chlorides)<sup>4</sup>, if the alkal cellulose is subjected to continual agitation during the etherifying process a higher ester is produced. By this means ethylcellulose containing 51-53 ethoxyl may be made. Aqueous insoluble esters of partially alkylated cellulose (mono- or di-, -methyl-, -ethyl- or -propylcellulose) are obtained by treating cellulose alkyl ethers which are soluble in or swelled by water<sup>5</sup>, with anhydrides or chlorides of organic acids in

1. I. G. Farbenindustrie, Akt.-Ges., K. Sponsel and G. Balle, D. R. P. 524509; abst. C. A. 1931, **25**, 4401; Nitrocellulose, 1931, **2**, #5, 104.

2. I. G. Farbenindustrie, Akt.-Ges., E. Pfeffer and E. Fischer, D. R. P. 525182, Addn. to 495712; abst. C. A. 1931, **25**, 4413. D. R. P. 495712, 451411.

3. I. G. Farbenindustrie, Akt.-Ges., L. Rosenthal and R. Hebermehl, D. R. P. 525424; abst. C. A. 1931, **25**, 4139; Nitrocellulose, 1931, **2**, #5, 104. Can. P. 310150.

4. I. G. Farbenindustrie, Akt.-Ges., O. Ernst, G. Balle and K. Sponsel, D. R. P. 525650, Addn. to 522575; abst. C. A. 1931, **25**, 4705; Nitrocellulose 1931, **2**, #6, 104. Can. P. 317262. Cites E. P. 200160. Aust. P. 92320.

5. I. G. Farbenindustrie, Akt.-Ges., G. Balle and K. Sponsel, D. R. P. 525835; abst. C. A. 1931, **25**, 4706; Nitrocellulose, 1931, **2**, #5, 104.

the presence of a catalyst. Methods are given for the preparation of methyl- and ethyl-cellulose acetate, benzoate, stearate and oleate. Cellulose ether silk which will successfully withstand boiling is prepared by dry-spinning cellulose ethers which are insoluble in ice-cold water or 10-30% ethyl alcohol. Example, ethylcellulose 10 (47% ethoxyl) dissolved in 50% spirit at room temperature, a mixture of benzene 40, spirit 2.5 added, filtered, and dry-spun in the usual manner<sup>1</sup>.

Facility in etherification and larger yields are said to result when the cellulose is first moistened, then stirred with dimethylaniline, then ethylated with ethyl chloride under pressure in the usual manner<sup>2</sup>. Transparent films and filaments of great tenuity and tensile strength result when a water-soluble methylcellulose is mixed with a water-insoluble substance capable of forming a colloidal solution (latex, phenol-formaldehyde, resin, linseed oil, or other water-soluble cellulose ether). Such films are substantially unaffected by water<sup>3</sup>. Simple or substituted saturated or unsaturated alkyl halide mixed with ethylene oxide or homologues<sup>4</sup>, when caused to react upon alkal cellulose in the presence of diluents or catalyzers gives rise to cellulose oxyethers, of which methods for producing benzyloxyethyl-, benzyloxybutyl-, propyloxyethyl- and chlorbenzyloxyethyl-cellulose are given<sup>5</sup>. Primary acetone-soluble hydroxyalkylcellulose acetates are prepared which are only slightly sensitive to water by treating alkal cellulose with ethylene oxide at temperatures below 30° and acetylating the prod-

1. I. G. Farbenindustrie, Akt.-Ges., and H. Henecka, D. R. P. 525860; abst. C. A. 1931, **25**, 4707; Nitrocellulose, 1931, **2**, #5, 104. Cites D. R. P. 511019.

2. I. G. Farbenindustrie, Akt.-Ges., and E. Huber, D. R. P. 526792; abst. C. A. 1931, **25**, 5030.

3. I. G. Farbenindustrie, Akt.-Ges., G. Balle and K. Sponsel, D. R. P. 527197; abst. C. A. 1931, **25**, 4705; Nitrocellulose, 1931, **2**, #8, 166. Cites D. R. P. 406681.

4. I. G. Farbenindustrie, Akt.-Ges., and C. Neubauer, D. R. P. 527403; abst. C. A. 1931, **25**, 4725.

5. I. G. Farbenindustrie, Akt.-Ges., M. Hagedorn and E. Rossbach, D. R. P. 527616; abst. C. A. 1931, **25**, 5288. Swed. P. 72244.

uct<sup>1</sup>. Example, cellulose is steeped in 26% NaOH for 6 hrs. and pressed to 3.75 (based on original cellulose), then suspended in propylene oxide for 6 hrs. at 16-17°. The hydroxypropylcellulose is then extracted with methyl alcohol and acetylated in the usual manner. Oxyethylcellulose and its acetate are similarly prepared. In the etherification of wood, it is treated with etherifying agents at an elevated temperature in the presence of alkalis<sup>2</sup>. Thus, a mixture of pinewood 1 and NaOH 50% solution 4, may be heated with ethyl chloride 3, at 100° for 6 hrs. The ethers formed retain the appearance of the wood, but are fusible and completely soluble in aromatic alcohols, acetone or methylene chloride. Pine wood or beech wood flour have likewise been transformed into ethyl-, ethylbenzyl- and benzyl celluloses.

Colored cellulose ether and ester lacquers and varnishes are formed by adding salts of sulfo- or carboxylic acid dyes with organic dye bases<sup>3</sup>, an example being Auramine base ground with the disazo dye from tetrazotized dianisidine and 1.8-aminonaphthol-2-4-disulfonic acid and alcohol. In reserve printing with aniline black or other colors produced by the oxidation of vat dyes in the fiber<sup>4</sup>, the printing reserve consists of vat dyes and solutions of cellulose ethers or esters precipitable by alkali to form a suitable thickening agent. A dye for cellulose ethers and esters results when 1.4-diamino-5.8-dihydroxyanthraquinone is heated with sulfuric acid and methyl alcohol<sup>5</sup>. The product gives blue-green shades, but can be separated by means of suitable solvents into two dyes, one of which gives pure green shades.

1. I. G. Farbenindustrie, Akt.-Ges., and M. Hagedorn, D. R. P. 527617; abst. C. A. 1931, **25**, 5287. Mentions U. S. P. 1502379. D. R. P. 363192.

2. I. G. Farbenindustrie, Akt.-Ges., and E. Teupel, D. R. P. 528359; abst. C. A. 1931, **25**, 4707.

3. I. G. Farbenindustrie, Akt.-Ges., K. Holzach and W. Mueller, D. R. P. 529840; abst. C. A. 1931, **25**, 5304. E. P. 330895.

4. I. G. Farbenindustrie, Akt.-Ges., and E. Pfeffer, D. R. P. 529969; abst. C. A. 1931, **25**, 5300.

5. I. G. Farbenindustrie, Akt.-Ges., P. Nawiasky and A. Krause, D. R. P. 531103; abst. C. A. 1931, **25**, 5575.



Plastic celluloid-like masses are produced by dissolving ethylcellulose 50 in a mixture of stearic acid 50 and ceresin 30 at 130°, carnauba wax 10 and a fat-soluble azo dyestuff 3 (parts) then being incorporated<sup>1</sup>. Water-insoluble binding agents of cellulose ethers and esters are formed without the aid of plasticizers or solvents<sup>2</sup>, the binding agents being dispersed in aqueous media. Example, nitrocellulose 100 is mixed with water 100 and methylcellulose 100 until a putty-like mass is formed. Then fillers and coloring matters are kneaded, the final product forming an excellent pore filler for woods, which is applied in the usual way through the addition of dilution agents. A lacquer is produced with much less than the usual amount of volatile organic solvent<sup>3</sup>, when a cellulose ether or ester is mechanically worked up with at least an equal weight of solid coloring matter until the latter is brought to practically a colloidal state of dispersion and the composition is in such a condition as to give a substantially non-settling solution with a lacquer solvent. This composition may be used alone or incorporated with a cellulose ester lacquer. Addition of 15-25% of low-leaded zinc oxide or tin oxide prevents "chalking" of cellulose ether or ester lacquers, which may contain dammar resin and butyl phthalate<sup>4</sup>.

In the formation of coating materials for floor coverings and plastic masses<sup>5</sup>, water-wet cellulose ethers or esters are incorporated with a non-volatile combined gelatinizer and plasticizer (butyl phthalate, camphor oils, *p*-toluenesulfamide) and, if desired, a softener, in quantities such that the weight of the plasticizer and softener together does not greatly exceed the dry weight of the cellulose derivative. The water which separates is poured off, and the

1. I. G. Farbenindustrie, Akt.-Ges., Swiss P. 143038.
2. *Ibid.* Swiss P. 145463; abst. Nitrocellulose, 1931, **2**, #8, 167.
3. C. Immerheiser and E. Knebel, U. S. P. 1830944. Cite U. S. P. 1589700.
4. Imperial Chem. Industries, Ltd., E. P. 356446; abst. J. S. C. I. 1931, **50**, 1019-B.
5. Imperial Chem. Industries, Ltd., and B. Foster, E. P. 348156 abst. J. S. C. I. 1931, **50**, 728-B. See also E. P. 331837.

remainder removed by heating. Cellulose glycol ethers which are soluble in water and insoluble in the common organic solvents are obtained by treating alkalicellulose<sup>1</sup>, with solid caustic soda and ethylene chlorhydrin and heating the mixture for about 8 hrs. at 100°. The cellulose ether when isolated from the yellow, sticky reaction mass by dialysis and subsequent precipitation with acetone, is obtained as a white, fibrous material readily soluble in water, giving a solution of high viscosity.

A process for the printing of fabrics containing cellulose ethers or esters has been granted patent protection<sup>2</sup>, using water-insoluble azo and nitro-substituted diphenylamine dyestuffs, characterized by adding to the printing paste hydroxyethylamines (triethanolamine). The colors recommended are of the "Dispersol" type (i.e. Dispersol Fast Orange A and BS, Dispersol Fast Yellow A).

A plastic composition of ethyl-, acetyl- or propionyl-cellulose is made by adding thereto acidyl derivatives of halogenated anilines (acetyl-, propionyl-, butyryl-chloraniline or -bromaniline)<sup>3</sup> in conjunction with usual volatile solvents as a succedaneum for celluloid. An opaque, washable playing card has been described<sup>4</sup>, comprising a sheet of alkylcellulose or alkylcellulose acetate 0.25-0.3 mm. thick, in which has been incorporated in amount sufficient to produce the degree of opacity desired, bismuth oxychloride or sub-nitrate, antimony oxide, mercurous chloride, titanium oxide or zinc sulfide being recommended. For safety (?) in use, the pigment is used in amounts sufficient to no longer allow light to pass through from a strong source of illumination. In the production of benzylcellulose, A. Lautenberg<sup>5</sup> has described an appliance for concentrating the

1. Imperial Chem. Industries, Ltd., and A. Levesley, E. P. 343873; abst. J. S. C. I. 1931, **50**, 480-B; Brit. Plastics, 1931, **3**, #28, 63.

2. Imperial Chem. Industries, Ltd., A. Shepherdson and L. Smith, E. P. 351056.

3. G. Schneider, Can. P. 317330.

4. S. Klausner, A. Eichengruen and R. Roehm, U. S. P. 1811322.

5. Belg. P. 375515. Ital. P. Dec. 21. 1929.

alkalicellulose prior to benzylation. Transfers are made from a paper base and a composition containing ethyl- or benzyl-cellulose<sup>1</sup>, a resinous material (ethyl abietate, cumar), and a high boiler (ethyl lactate, diethylene glycol monoethyl ether). In the A. Liebster method for producing cellulose ethers<sup>2</sup>, raw cellulosic material which has been predigested with dilute alkali, washed neutral with water and dried, is treated with a slight excess of concentrated alkali and the resulting unripened alkalicellulose etherified with rather more than the theoretical amount of ethyl chloride, forming triethylcellulose. L. Lilienfeld also dries the alkalicellulose before etherification<sup>3</sup>, but specifies that the temperature of drying shall be under 18°.

Alkali-soluble alkyl derivatives of cellulose are prepared by treating alkali-soluble conversion products or derivatives of cellulose with an alkylating agent in such an amount that not more than 1 mol. of alkylating agent (preferably 0.35-0.66 mol.) is present for each cellulose molecule<sup>4</sup>. Threads or other artificial products are made by coagulating a solution of the xanthate of an O-oxyalkylcellulose (oxyalkylcellulose xanthate) made into the desired form. If viscose is treated with glycol- or glycerol-trithiocarbonate, filaments formed therefrom are coagulated by 50% sulfuric acid, and in either the wet or dry state have a high resistance<sup>5</sup>. If cellulose, linen, flax, jute or hemp is treated with an alkylating agent (methyl or ethyl sulfate, methyl or ethyl bromide or iodide, benzyl chloride), in the presence of benzene, chloroform or carbon tetrachloride, and sodium hydroxide, methyl-, ethyl- or benzyl-ethers result without apparent change in structural form of the cel-

1. W. Lawrence and Kaumagraph Co., E. P. 338611; abst. C. A. 1931, **25**, 2532.

2. E. P. 355563; abst. J. S. C. I. 1931, **50**, 1006-B.

3. U. S. P. 1683682; abst. C. A. 1928, **22**, 4246.

4. *Ibid.* D. R. P. 521452; abst. C. A. 1931, **25**, 2847. Cites D. R. P. 323891.

5. L. Lilienfeld, F. P. 700535; abst. C. A. 1931, **25**, 3833. Cites E. P. 231807. Addn. 35752 to F. P. 664416; 676756, 679149, 700534, 700545. D. R. P. 527254, Addn. to 467003.

lulose operated upon<sup>1</sup>. New cellulose derivatives containing alkyl groups and soluble in aqueous alkali but insoluble in water are prepared by heating cellulose insoluble in alkali with an amount of NaOH not exceeding 75% of the weight of the dry cellulose used, in the presence of an alkylating agent. Thus, 200 parts of sulfite cellulose are treated with 100 of powdered caustic soda and ethyl chloride 160 in an autoclave at 100-110°<sup>2</sup>.

In the preparation of cellulose ether and ester enamels<sup>3</sup>, a suspension of a pigment in liquid is centrifugally forced into a more or less compressed mass of cellulose ether, moistened with a liquid with which the pigment-suspending liquid is miscible. Hexachlorethane has been patented as a combustion preventative for cellulose ether or ester compositions associated with an aromatic phosphate<sup>4</sup>. Laminated glass<sup>5</sup> that is shatterless is formed when acetyl-, propionyl-, butyryl-, methyl-, ethyl- or benzyl-cellulose is admixed with a polymerized vinyl compound and acetin, interposed between two or more glass sheets, and heat and pressure applied. Vinyl alcohol, acetate or chloracetate, or styrene are recommended. A. Müller<sup>6</sup> has investigated the ring structure of *b*-methylgalactoside, and prepared the 6-triphenylmethyl ether, 2,3,4-triacetate, 2,3,4-tribenzoate and 2,3,4-tribenzoyl-*b*-methylgalactoside 6-*p*-toluene sulfonate, mainly of theoretical interest.

A dry glue in the form of powder or flakes has been described<sup>7</sup>, consisting of two interpenetrative components, one of which is a cellulose ether, and each of which is an adhesive under the influence of a solvent. Examples, (1) ethylcellulose, ethylacetanilide and vinyl acetates; (2) ace-

1. L. Lilienfeld, U. S. P. 1800944; abst. C. A. 1931, **25**, 3498.
2. *Ibid.* D. R. P. 521453, Addn. to 496978; abst. C. A. 1931, **25**, 4401.
3. A. Martin, E. P. 354748; abst. J. S. C. I. 1931, **50**, 1019-B.
4. W. Lindsay, U. S. P. 1630752; abst. C. A. 1927, **21**, 2384.
5. W. Moss, U. S. P. 1831462.
6. Ber. 1931, **64-B**, 1820; abst. J. S. C. I. 1931, **50**, 1039-A.
7. R. Mueller and W. Stelkens, F. P. 701353; abst. C. A. 1931, **25**, 4097. See also F. P. 677253.

tylcellulose, artificial resin and benzenesulfamide. Piperidine (hexahydropyridine) has been advocated as a desirable cellulose ether plasticizer in conjunction with acetone<sup>1</sup>. Likewise *p*-anisidine<sup>2</sup>. In an investigation involving structure-viscosimetric measurements of cellulose derivatives in organic solvents and the influence of additions on their viscosity<sup>3</sup>, determinations with the overflow viscosimeter show that sols of ethylcellulose in acetone, benzyl alcohol and mixtures of ethyl alcohol with ethyl ether exhibit structure viscosity, the strongest effects being observed in ethyl alcohol-benzene mixtures. As a rule, the structure viscosity increases with the addition of a medium having a pronounced solvent power. In the production of electrical insulation materials<sup>4</sup>, benzylcellulose with a relatively large proportion of plasticizers as 20-30% triaryl or trialkyl phosphate and ethyl or butyl tartrate or phthalate is claimed. H. Okada has found that alkalicellulose reacts more uniformly with benzyl chloride than with ethyl chloride, a product almost completely soluble in benzene being obtained by one-stage benzylation, by immersion of cellulose in NaOH 30-50%, pressing free from excess alkali and treatment with benzyl chloride at 100°. By a two-stage benzylation an ether completely soluble in benzene can be obtained<sup>5</sup>. Use of benzene or toluene reduces reaction velocity, and temperatures below 100° cause depolymerization of cellulose rather than etherification. In comparison with nitrocellulose film, benzylcellulose film has a greater elasticity but lower tensile strength. A sharp division is noticeable in carbon percent in products soluble completely in pure benzene and those only soluble in benzene containing alcohol.

1. T. Murray and C. Staud, U. S. P. 1826667.

2. *Ibid.* U. S. P. 1826668.

3. Y. Nisizawa, Kolloid-Z. 1931, **56**, 59; abst. J. S. C. I. 1931, **50**, 1008-A.

4. Non-Inflammable Film Co., Ltd., and V. Yarsley, E. P. 355654; abst. J. S. C. I. 1931, **50**, 1016-B.

5. H. Okada, Cellulosechemie, 1931, **12**, 11; abst. C. A. 1931, **25**, 5759.

Pure cellulose and etherified lignin may simultaneously be obtained from such materials as straw, bamboo, esparto or other non-ligneous vegetable materials by alcoholysis in an acid medium, practically all the lignin being rendered soluble, the remaining cellulose being readily separable by filtration therefrom<sup>1</sup>. Example, chopped barley straw or esparto 100 are added to ethyl alcohol 1000 with ethyl bromide (or HCl gas) 20. The mixture is then heated to about 150° in an autoclave for 2 hrs. under 11-12 atm. After filtering the alcoholic solution from the precipitate (pure cellulose 40-45), the filtrate is freed from the major portion of alcohol by distillation, poured into dilute acid whereby bright brown flakes of ethylated lignin are obtained. Likewise methylcellulose and benzylcellulose may be prepared. Wood oil, the product resulting from the distillation at a maximum temperature of 120° of residual oil obtained in the initial distillation of wood and containing methyl alcohol, acetone, allyl alcohol, furfural, ethyl alcohol, dimethyl acetate and pyroxanthine<sup>2</sup>, has been patented as a direct cellulose ether solvent.

E. Pfeffer<sup>3</sup> has described a process for printing with vat colors in which methylcellulose ("Thickening M") in 10% solution in water is used as the thickening agent. In coating sheets of cellulose ether or ester material with metals as silver, the sheets are superficially reduced by treatment with mineral acid to liberate free cellulose<sup>4</sup>, then reacting on the cellulosic portion with ammoniacal silver nitrate solution to produce a metallic deposition, particularly advantageous in the coating of insulating plates used in electric condensers. Bronze 3-4, to 7 of a 20% solution of a mixture of ethyl- and nitro-cellulose (2:1) in the usual solvents<sup>5</sup>, with plasticizer up to 5%, is used for wrapping.

1. K. Ott and H. Schuessler, U. S. P. 1806703.

2. M. Ow-Eschingen, U. S. P. 1794066. Compare E. P. 28611896.

3. U. S. P. 1744140. See D. R. P. 241997.

4. E. Pfiffner, U. S. P. 1744281; abst. C. A. 1930, **24**, 1508.

5. E. Richter, U. S. P. 1816398.

the coil tip of a cigarette, it being claimed that such coils do not collect electrostatic charges even when the film itself is not made antistatic.

F. Schmidt<sup>1</sup> has described a process for producing artificial horn consisting in first mixing about 30 parts of ethyl- or benzyl-cellulose with alcohol 20 and water, then mixing separately casein 60 with water 10 and alcohol 5, kneading together the two mixtures to a moldable mass. In protecting leather, skins and fabrics during their manipulation into fully fabricated goods as fancy leather articles<sup>2</sup>, they are protected from soiling during making up, by applying a film of benzylcellulose, which film is stripped off when ready for sale. To produce etherified cellulose with the minimum of reactants<sup>3</sup>, cellulose 100 is moistened with water 50 and dry NaOH 200 added and thoroughly mixed. This is charged into an autoclave with ethyl chloride 400 and heated 24 hrs. at 90-170° (some range), the ethylcellulose thus produced being insoluble in water and "of the high quality necessary for the production of transparent compositions which may be employed in film and varnish making."

Artificial filaments are obtained by spinning a solution of dissolved methyl-, ethyl- or benzyl-cellulose with an artificial resin obtained by the condensation of formalglycerol and a hydroxyaromatic alcohol (hydroxybenzyl-, tolyl or -xylyl alcohol) in the presence of a high boiler as diphenylol propane<sup>4</sup>. Arylaminoanthraquinones are made by heating with boric acid and a primary aromatic amine the leuco derivative of a hydroxyanthraquinone, or of an amino or alkylamino derivative in aqueous solution or suspension. The products, if non-sulfonated, dye cellulose ethers green

1. U. S. P. 1811972; abst. C. A. 1931, **25**, 4983. E. P. 230025; abst. Chem. Zentr. 1925, II, 624. Swiss P. 113925.

2. Etabl. R. Schneider and A. Poelman, E. P. 344453; abst. J. S. C. I. 1931, **50**, 601-B.

3. P. Seel, W. Webb and J. Donohue, U. S. P. 1813665; abst. C. A. 1931, **25**, 5288.

4. G. Seymour, U. S. P. 1828449.

or blue<sup>1</sup>. In the printing of fabrics and textiles of or containing cellulose ethers, aminoanthraquinonesulfonic acids are used<sup>2</sup>, as sulfonated 4-benzylamino-1-methylaminoanthraquinone (blue), 1-amino-4-*p*-acetamidoanilinoanthraquinone-3-sulfonic acid (blue), 4-8-diaminoanthraquinone-2-sulfonic acid (blue), 1-4-di(2'-sulfo-*p*-toluidine)anthraquinone (green), 1-amino-4-hydroxyanthraquinone-5-sulfonic acid (red-violet), and 1-aminoanthraquinone-5-sulfonic acid (orange); these colors do not sublime during the process.

New cellulose ethers have been described obtained by treating alkal cellulose with cyanuric chloride or bromide, dichlorquinazoline, dichlorphthalazine, tribrompyrimidine or the dichloride of maleic acid hydrazide<sup>3</sup>, the treated products—especially if in the first stage alcoholic NaOH solution is used—are immune to cotton dyes and possess an affinity for basic dyes. Material as cotton yarn is treated with caustic soda and allyl bromide under such conditions that the formation of allylcellulose does not lead to the loss of fibrous structure or a diminution in strength of the original fiber. The cotton increases 17-18% in weight by the etherification and is immune to direct dyes but may be dyed with basic dyes<sup>4</sup>. Another method for improving the affinity of cellulose derivatives to acid dyes<sup>5</sup>, is impregnation of the cellulose with alcoholic caustic potash solution, then xanthate with carbon bisulfide with simultaneous or subsequent treatment with a cyanogen halide in benzene in the presence of an organic base.

Greenish-yellow shades are obtained on cellulose ethers and esters in textiles or varnishes by use of the dyes *p*-alkox-

1. Soc. Chem. Industry in Basle, E. P. 338412; abst. C. A. 1931, **25**, 2302.

2. *Ibid.* E. P. 341419; abst. C. A. 1931, **25**, 5043; J. S. C. I. 1931, **50**, 438-B. Cites D. R. P. 420974, 433236. E. P. 282853.

3. *Ibid.* E. P. 342167; abst. C. A. 1931, **25**, 5030.

4. *Ibid.* E. P. 342689; abst. C. A. 1931, **25**, 5578; J. S. C. I. 1931, **50**, 485-B. E. P. 234847, 317019.

5. *Ibid.* E. P. 343748; abst. J. S. C. I. 1931, **50**, 480-B.



yaniline with *p*-cresol<sup>1</sup>. Example, 4'-methoxy (or ethoxy) 2-oxy-5-methylazobenzene. Cellulose derivatives are obtained by treatment of alkal cellulose with a heterocyclic compound containing one or more N:C-halogen groups, then further treated with a compound containing an imido, or hydroxy rest, which induces in the cellulose compound a pronounced affinity for acid dyestuffs<sup>2</sup>. Regenerated cellulose or partly etherified cellulose may be esterified without loss of structure or degradation of the cellulose aggregate by impregnating the material with potassium acetate or other potassium salt of a weak acid, drying and heating with an organic acid anhydride, optionally with addition of esterification accelerators, but without addition of acid catalysts. The products contain between 1 and 2 acetyl groups per C<sub>6</sub> cellulose, show the dyeing properties of acetate silk, are insoluble in organic solvents, have a high wet strength and may be obtained either as mat woolly fibers or as highly lustrous smooth fibers<sup>3</sup>.

Fast shades are obtained on cellulose ethers and esters by means of 1-methyl (or ethyl) amino-4-anilinoanthraquinone (greenish-blue)<sup>4</sup>. A new cellulose derivative is prepared by acting on alkal cellulose in the presence of acid-binding agents, with 1-*b*-chlor (or brom) ethylpiperidine<sup>5</sup>. In order to diminish the denier of ethylcellulose filaments<sup>6</sup>, they are passed through a chamber where the vapor of chloroform or other swelling agent is encountered, the threads being simultaneously submitted to traction. In the

1. Soc. Chem. Industry in Basle, E. P. 344884; abst. J. S. C. I. 1931, **50**, 674-B. Cf. E. P. 263579, 269934, 271898.

2. *Ibid.* E. P. 347926, Addn. to 342167; abst. Silk J. 1931, **8**, #89, 54.

3. *Ibid.* E. P. 353978; abst. J. S. C. I. 1931, **50**, 921-B.

4. *Ibid.* F. P. 697541; abst. C. A. 1931, **25**, 3176. Compare F. P. 568655.

5. *Ibid.* Swiss P. 145053, Addn. to 141556; abst. C. A. 1931, **25**, 5287.

6. Soc. pour la Fabrication de la Soie "Rhodiaseta," F. P. 705359; abst. C. A. 1931, **25**, 5287. D. R. P. 508070; abst. C. A. 1931, **25**, 814; Chem. Zentr. 1930, II, 3104. Swiss P. 131560; abst. Chem. Zentr. 1929, II, 1755.

formation of polychromatic screens for color photography<sup>1</sup> films of cellulose ether or ester are coated with an azo-dye constituent. Lines or other geometrical patterns are then printed on the surface with compounds forming differently colored azo dyes. Thus, a film is soaked in an alcoholic NaOH solution of diazotized *b*-naphthylamine and a solution of diazotized dianisidine to produce a multicolor effect.

A lacquer which forms clear, adherent coatings of high suppleness is formed when water-insoluble ethylcellulose 5 is dissolved in a mixture of isobutyl acetate 50, toluene 25, ethyl alcohol 18 and ethylene glycol monophenyl (or cresyl or propyl) ether 1-2 parts<sup>2</sup>. By means of double decomposition (yellow from lead acetate and acid potassium bichromate) pigments may be produced in dissolved cellulose ethers or esters in such finely divided form that when the material is allowed to stand, the formed pigment is so finely dispersed that grinding is unnecessary<sup>3</sup>. In the manufacture of permanently transparent, flexible, substantially waterproof films of desired thinness<sup>4</sup>, a cellulose ether or ester is combined with a di(or tri or tetra)glycol monoalkyl ether (where "alkyl" is methyl, ethyl, propyl, butyl or amyl) of phosphoric acid, an example being the monoethyl ether of tetraethyleneglycol phosphate.

The viscosity of cellulose ethers (as ethylcellulose of 40% ethoxyl) is diminished without degradation or change in solubility by heating with an acid as acetic or hydrochloric acids or sodium acid sulfate. Example, ethylcellulose 1 of 800 viscosity<sup>5</sup>, is heated 0.6-6 hrs. at about 95° with 80% acetic acid 5-20 parts. Viscosity after 15 minutes treatment 445; after 5 hrs. 62; after 6 hrs. 50. The material is then washed and dried. The manufacture of cel-

1. Spicers, Ltd., D. R. P. 525611; abst. C. A. 1931, **25**, 4477.
2. G. Steimmig, U. S. P. 1788781; abst. C. A. 1931, **25**, 1083.
3. E. de Stubner, U. S. P. 1795764; abst. C. A. 1931, **25**, 2566.
4. A. Sulzer, U. S. P. 1826681.
5. A. Wacker Gesellschaft fur Elektrochemische Ind. G. m. b. H., E. P. 342391; abst. C. A. 1931, **25**, 5557; J. S. C. I. 1931, **50**, 388-B. A. Ascherl and W. Gruber, U. S. P. 1834040.

lulose ethers with low boiling alkylating agents (methyl or ethyl chloride) involves the use of pressure containers for conducting the operation. It is proposed to add a carbonate (sodium, potassium, calcium, barium) to the etherifying mixture of alkal cellulose and alkylating agent<sup>1</sup>, CO<sub>2</sub> being set free at the close of alkylation of alkal cellulose, and this may be readily recognized and the course of the reaction correspondingly governed.

Finished artificial filaments, yarns or films of cellulose ethers or esters which have been treated with a neutral organic swelling agent (as dioxane)<sup>2</sup>, are gradually stretched 200% up to over 1000% while still in contact with the swelling medium. Previous to, during, or immediately after these operations the threads may be subjected to transverse pressure, e.g., by rolling, being finally treated with salt solution, washed with water and dried. By the action of monochlorodimethyl sulfate, dichlorodimethyl sulfate, or chlormethoxysulfonyl chloride on alkal cellulose<sup>3</sup>, cellulose monomethylene ether is obtained, following the technique of Haworth for the methylation of sugars. The cellulose ether is fibrous in structure, very inert, stable to alkalis but not to acids, thus resembling the acetone-sugars. Cellulose monomethylmonomethylene ether may be esterified and etherified. E. Worden<sup>4</sup> has described an alpha-cellulose obtained from fiber of the *Musa* species as being especially adapted for etherification and esterification purposes on account of its abnormally high tensile strength.

In a determination of the space groups of certain carbohydrates<sup>5</sup>, J. Young and W. Spiers find the process of

1. A. Wacker Gesellschaft fur Elektrochemische Ind. G. m. b. H., A. Ascherl and W. Gruber, D. R. P. 520384; abst. C. A. 1931, **25**, 2847. F. P. 703338; abst. C. A. 1931, **2**, 4401. Cites D. R. P. 408342, 435346, 488780, 494917, 499129. E. P. 200827, 305946. U. S. P. 1694127.

2. K. Weissenberg and B. Rabinowitsch, E. P. 352445; abst. J. S. C. I. 1931, **50**, 878-B.

3. F. Wood, J. S. C. I. 1931, **50**, 411-T.

4. U. S. P. 1814106. Can. P. 298172.

5. Zts. Krist. 1931, **78**, 101.

methylation does not appreciably alter the *c*-spacing, the spacing of 4.5 Å. in the principal dimensions of the unit cells being of frequent occurrence. The synthesis and properties of 1-*b*-methyl gentiobiose, 1-*b*-methyl-6-*α*-glucosidoglucose and 1-*b*-methylgentiobioside heptabenzoate have been published<sup>1</sup>. The manufacture, properties, solubilities and applications of benzylcellulose have been described<sup>2</sup>. An apparatus for cutting thin sheets of cellulose ether or ester comprises a cable connected to the leads of a low voltage alternating circuit along the length of a knife<sup>3</sup>. The rapidly changing magnetic field due to the current in the cable heats a steel bar in contact with the knife, this method permitting temperatures up to about 200°.

In order to obtain cellulose ether plastic bodies, a solution is formed by heating with a polyhydric alcohol as ethylene glycol, and is<sup>4</sup> extruded through a suitable nozzle and coagulated either by cooling or by passage through a liquid (water or a polyhydric alcohol) which is maintained above room temperature and contains a solvent or plasticizer for the cellulose derivative, or<sup>5</sup> cooled, freed from part of the alcohol, and crushed to yield a molding powder. In the formation of creped textile materials<sup>6</sup> the cellulose ether or ester filaments are coated either with a layer of cellulose, e.g., by surface hydrolysis or by coagulation of viscose or cuprammonium cellulose solution, or with another cellulose ester or ether in which the esterifying or etherifying radicals contain hydroxyl or carboxyl groups as cellulose acetate tartrate, and after highly twisting and weaving with other fibers, the resulting fabric is scoured with water or soap solution to cause swelling of the coating.

1. G. Zemplén and Z. Bruckner, Ber. 1931, **64-B**, 1852; abst. J. S. C. I. 1931, **50**, 1040-A.

2. Nitrocellulose, 1931, **2**, #3, 58.

3. F. Small and W. Dickie, U. S. P. 1637715.

4. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 355298; abst. J. S. C. I. 1931, **50**, 1044-B.

5. British Celanese, Ltd., W. Dickie and P. Sowter, E. P. 355330; abst. J. S. C. I. 1931, **50**, 1044-B.

6. British Celanese, Ltd., H. Dreyfus, W. Dickie and C. North, E. P. 357169; abst. J. S. C. I. 1931, **50**, 1090-B.

The luster of materials of cellulose ether or ester may be increased or rendered more uniform by subjecting to the action of steam superheated about 20°. The steam is preferably at super atmospheric pressure, and the degree<sup>1</sup> of superheat may vary up to 100°. As a cellulose ether plasticizer<sup>2</sup>, a resinous reaction product of pentaerythrite and mono-, di-, tri-, tetra-, or hexa-hydroxystearic acid or dihydroxybenhenic acid has been recommended. Yarns or filaments of cellulose ether or ester may be conditioned by means of a combined softening and lubricating agent<sup>3</sup>. Suitable softening agents are ethylene- or propylene-glycol, glycerol, toluene and xylene. The lubricants used are vegetable oils as castor or olive, or animal oils as neatsfoot, to which ethyl or butyl alcohol may be added. Or the yarns may be subjected to successive treatments comprising the application for identification purposes of a liquid containing a fugitive coloring matter (i.e., one having no affinity for the fiber) and a lubricating liquid<sup>4</sup>.

Hollow cellulose ether filaments are produced by using spinning dies, the holes of which are of conical shape and taper on the outside face of the die<sup>5</sup>. An artificial leather has been described in which the groundwork is composed of ethylcellulose<sup>6</sup>. S. Carroll<sup>7</sup> advocates the use of trimethylene glycol dibutyrate as a cellulose ether or ester plasticizing body, and J. Davidson<sup>8</sup> certain alkyl benzenes (monoethyl-, diethyl-, hexaethyl-, -butyl-, -propyl-, -pentyl-benzene).

1. British Celanese, Ltd., G. Ellis and H. Olpin, E. P. 349980; Addn. to E. P. 332231; abst. Silk J. and Rayon World, Nov. 1931, **8**, #90, 62.

2. H. Bruson, U. S. P. 1835203.

3. British Celanese, Ltd., E. P. 351084; abst. Textile Mfr. 1931, **57**, 458.

4. British Celanese, Ltd., E. P. 350056; abst. Silk J. and Rayon World, 1931, **8**, #91, 54.

5. Cellulose Acetate Silk Co., Ltd., and H. Curtis, E. P. 353041; abst. Textile Mfr. 1931, **57**, 461; J. S. C. I. 1931, **50**, 878-B.

6. Compagnie Francaise D'Exploitation Des Procedes Plinatus, F. P. 664888; abst. Kunst. 1931, **21**, 213.

7. U. S. P. 1836701.

8. U. S. P. 1834050.

In the process of producing open work fabrics of predetermined design<sup>1</sup>, methyl-, ethyl- or benzyl-cellulose yarn is treated with a mineral acidic carbonizing promoting compound, and the fabric then subjected to a carbonizing temperature. Differential effects are also producable by spinning short lengths of cellulose ether yarn with vegetable fibers, and then carbonizing the vegetable fibers out of the mixed spun yarn<sup>2</sup>. In the production of sheet materials having a basis of cellulose ethers and esters<sup>3</sup>, a homogeneous mixture of the cellulose derivative with a plasticizer is rendered fluid by heat in the substantial absence of volatile solvents, and is drawn off through an adjustable aperture in the heating tank between two similar water-cooled rolls rotated synchronously in opposite directions. The resulting sheets are conditioned by means of gases (moist air) and solvent vapors and cut to the desired shape.

It has been found that bright green shades may be produced on cellulose ethers and esters by the use of the compound (presumably) N.N'-dimethylindigo<sup>4</sup>, first described by L. Ettinger and P. Friedlander, applied directly in aqueous suspension in the presence or absence of protective colloids or dispersing agents<sup>5</sup>. Cellulose ester lacquers are formed by combining polymerization products of vinyl chloride with vinyl acetate, being soluble in benzene, toluene and butyl acetate<sup>6</sup>.

C. Dreyfus has patented as suitable fire retardants for methyl-, ethyl-, and benzyl-cellulose halogen substituted aromatic esters, trichlor (or brom or iodo), -phenyl (or cresyl, or xylenyl or naphthyl) formate, acetate or propionate<sup>7</sup>. In reducing the luster of cellulose ether textile materials<sup>8</sup> at least a part of the surface is treated with an ethanalamine

1. C. Dreyfus, R. Dort and H. Platt, U. S. P. 1834339.
2. C. Dreyfus, R. Dort and H. Platt, U. S. P. 1834388.
3. H. Dreyfus, E. P. 355732; abst. J. S. C. I. 1931, **50**, 1045-B.
4. A. Davidson, U. S. P. 1836155.
5. Ber. 1912, **45**, 2074; abst. C. A. 1912, **6**, 2760.
6. J. Davidson, U. S. P. 1838368.
7. U. S. P. 1838078.
8. C. Dreyfus and H. Platt, U. S. P. 1836527.

(mono-, di-, tri-ethanolamine) in the presence of water. Varying degrees of resistance to delustering of methyl- or benzyl-cellulose fabrics may be produced<sup>1</sup> by differential application to the fabric of the delustering agent, or by knitting into fabric form two yarns, one of which is more susceptible or resistant to delustering than the other.

By dry-spinning a solution of cellulose ether in a volatile solvent (acetone) with about 30% of high boiler (diacetone alcohol)<sup>2</sup>, into an evaporative medium containing vapors of a non-solvent for the cellulose ether (water or ethyl alcohol) pleasing differential effects are said to be possible.

Cellulose ethers and esters may be dyed greenish yellow tints of high fluorescence from compounds obtainable by the union of 4-amino-1.8-naphthalic anhydride with such bodies as methylamine, aniline, cyclohexylamine, and methyl- and dimethyl-aminobenzenes<sup>3</sup>. R. Haller and A. Heckendorn<sup>4</sup> have described the manufacture of cellulose ethers in the fibrous form containing sulfur, prepared by the action of chloracetic ester or allyl bromide and carbon bisulfide upon alkalicellulose, and then warmed with piperazine, diethylenediamine, aniline, dimethyl-*p*-phenylenediamine or ethylenediamine. The products have an outstanding affinity for acid dyestuffs. Cellulose ethers and esters may be dyed in yellow shades with the sulfamic acid of a 4-amino-1.8-naphthalic imide or substituted imide, as ethylimide, phenylimide or 4-*m*-xylylimide<sup>5</sup>. As solvents and plasticizers for the cellulose esters and ethers, mono-, di-, and tri-ethylpentaerythritol, which are pale yellow oils, have been patented<sup>6</sup>. Non-phototropic yellow shades are obtained on the cellulose ethers by application of 4-chlor-3-nitro-*o*-tolui-

1. C. Dreyfus and W. Whitehead, U. S. P. 1838663. H. Dreyfus, F. P. 37906 Addn. to F. P. 686644; abst. C. A. 1932, **26**, 318. See p. 197, note 5.

2. H. Dreyfus, E. P. 358500; abst. J. S. C. I. 1932, **51**, 17-B.

3. W. Eckert and C. Mueller, U. S. P. 1836529.

4. U. S. P. 1833038.

5. I. G. Farbenindustrie, E. P. 352099 Addn. to E. P. 304739; abst. J. S. C. I. 1930, **49**, 506-B; 1931, **50**, 1046-B.

6. Imperial Chemical Industries, Ltd., E. P. 358393; abst. J. S. C. I. 1931, **50**, 1135-B.

dine or 5-nitro-*m*-4-xylydine<sup>1</sup>. A benzylcellulose of uniform low viscosity substantially free from highly degraded products is produced by heating a high viscosity ether with dilute HCl under pressure (20-50 lb. per sq. inch)<sup>2</sup>. A superior coating composition of this ether results upon above heating with dilute acid to a viscosity of 0.1-5.0 c. g. s units in 10% solution in toluol-alcohol (4:1), which is then incorporated with plasticizer and volatile solvent<sup>3</sup>.

1. Imperial Chemical Industries, Ltd., S. Thornley and A. Twemlow, E. P. 353878; abst. J. S. C. I. 1931, **50**, 1137-B.

2. Imperial Chemical Industries, Ltd., D. Traill and A. Levesley, E. P. 352999; abst. J. S. C. I. 1931, **50**, 1089-B. D. Traill, Can. P. 319056.

3. Imperial Chemical Industries, Ltd., D. Traill and A. Levesley, E. P. 357123; abst. J. S. C. I. 1931, **50**, 1107-B.















